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A. M. Butlerov's DOCTORAL DISSERTATION: "ESSENTIAL OILS"*

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A.M.Butlerov's doctoral dissertation, "Essential Oils", is of considerable interest to historians of chemistry, since it contains in embryo the characteristic traits of Butlerov's scientific genius: breadth of generalization, depth of thought, and an endeavor to pose, if not to solve, the basic problems of organic chemistry.

This dissertation was never published, but has come down to us only in lithographed form; one of the copies is preserved in the Library of the M.I.Kalinin Polytechnic Institute in Leningrad.

Most likely because the dissertation was never printed, neither his contemporaries nor his biographers nor the researchers into Butlerov's scientific heritage quote its contents, confining themselves either to a formal mention of it or devoting a few words to the history of its defense.

N.A.Menshutkin, for example, in his recollections of Alexander Mikhailovich Butlerov says frankly:"I do not know A.M.Butlerov's master theses or doctoral dissertation." [1]

G.G.Gustavson and V.V.Markovnikov, who wrote lengthy articles on Butlerov's scientific work, make no mention of this dissertation, while A.M.Zaitsev, Butlerov's oldest pupil and one of the foremost Russian chemists, describes the defense of this dissertation in his biographical sketch of Butlerov's life and work and adds: "this dissertation was not available to me." [2]

In the spring of 1853, the young Butlerov (he was 25 years old at the time) submitted a dissertation entitled "Essential Oils" to the Faculty of Physics and Mathematics of the University of Kazan for the degree of doctor of chemistry and physics.

The reviewers' opinions of the merits of the dissertation differed. M.Ya. Kittary, professor of technology, together with P.I.Vagner, professor of mineralogy, considered it worthy of a conferral of the degree of doctor of physics and chemistry, but Savelyev, professor of physics, did not agree and suggested that the faculty submit it to another university for consideration.

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*A lecture delivered on October 5, 1950 at a joint meeting of the General Chemistry Section of the Leningrad Branch of the D. I. Mendeleyev All-Union Chemical Society and the Leningrad Branch of the USSR Academy of Sciences Commission on the History of Chemistry.

The Faculty of Physics and Mathematics of the University of Kazan agreed with Prof. Savelyev and decided to send the dissertation to another university for examination. This led Butlerov to withdraw his dissertation, and at the end of 1853, having received a prolonged leave, Butlerov went to Moscow, where he submitted his dissertation "Essential Oils," to the Faculty of Physics and Mathematics of the University of Moscow on January 16, 1854. Butlerov passed his doctoral examination brilliantly, defended his dissertation, and was granted the degree of doctor on June 4, 1854.

It is an interesting fact that Butlerov turned to his teacher, K.K.Claus (who had left Kazan by then and had transferred to Dorpat) for advice as to where he should go to defend his dissertation.

The A.M.Butlerov archives preserved in the Archives of the USSR Academy of Sciences in Leningrad, contain unpublished letters from Claus to Butlerov. Among them is a letter dated August 11, 1853, in which Claus writes: "Since you ask my advice, whether it is better to take the doctoral examination in Petersburg, Moscow, or Dorpat, my advice is to wait a while. But if there is no change, go to Moscow, where you will find in Lyaskov* a man who will help you with advice and actively. It would be hard for you to pass the examination in Dorpat, since the professor of physics is extremely demanding. But all this probably won't be necessary, inasmuch as you will attain your goal without difficulty in Kazan. Festina lente."**

Butlerov most likely followed Claus's advice. He esteemed Claus highly and had profound respect for him. In the obituary of N.K.Zinin, Butlerov wrote as follows about Claus in 1880 (more than 25 years later):

"Nor can I recollect this old teacher of mine except with deep gratitude. K.K. Claus was then about 50 years old, but he conveyed his dual love of chemistry and botany with a truly youthful ardor..." [3]

In another letter Claus regrets that A.M.Butlerov has written him nothing about how matters stood with the defense of his dissertation, writing:

Dorpat, May 12.

"Dear Alexander Mikhailovich:

"So be it, I shall write in Russian; it seems this will be pleasanter for you, not because you will have occasion to laugh at me, but because the Russian language is better for friendly communications.

"First of all, I congratulate you on your doctor's degree, which puts you on a par with other colleagues and entitles you to a chair of your own. I am glad, very glad, and congratulate you again. My only regret is that you did not write me the details of your examination, which interests me so much. You don't say a word about the examiners, your opponents, the dispute, how it all went, and how you like the University of Moscow and its scientists. Have you gotten to know Lyaskov, and have you found any other chemists there besides him?

"Second, I enclose a published article on the oil of Pulegium [4], which I received from the Academy some time ago. As I read it, the thought entered my mind that it is about time now for you to start doing something about printing a little paper in order to obtain the rank of associate professor, in order to prove to your malevolent colleagues that they are fools. What sort of faces do Savelyev and Popov make when they look at you now?"***

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*N. E. Lyaskov.

**Archives of the USSR Academy of Sciences in Leningrad, Collection 22, Catalog 2, No. 111.

***Ibid., Collection 22, Catalog 2, No. 112.

It may be supposed that Butlerov even chose the theme of his dissertation under the influence of his teacher Claus, who was not only a prominent chemist, but a botanist as well, as Butlerov mentions in his characterization of Claus quoted above. In his dissertation Butlerov states that he chose for chemical investigation " a plant discovered by Professor Claus in the Southern steppes along the Volga, which he has named Pulegium deserticola, containing a special essential oil, the chemical constitution of which is quite remarkable" (cf Dissertation, Par. 25).

In his recollections of Butlerov, A.M.Zaitsev writes:

"Upon his return to Kazan after having defended his dissertation, A.M.Butlerov published a paper in the St. Petersburg Academy Bulletins (XII, 241) on an essential oil from the plant Pulegium micranthum (Claus), growing in the southern stretches of Russia."

Zaitsev adds in parentheses:

"This experimental research probably represents an extract from his doctoral dissertation; I cannot assert this positively, since this dissertation was not available to me." [5]

It is an interesting circumstance that Zinin knew of this research of Butlerov's even before he defended his dissertation, as well as the question of the publication of his paper by an academic press.

In the Archives of the Academy of Sciences I have found an unpublished letter from N.N.Zinin to A.M.Butlerov. In the letter, dated December 5, 1853, Zinin writes:

"I am sending you, dear Alexander Mikhailovich, a note by Julius Fedorovich Fritzsche; answer it soon - you will see on page two of the enclosure the form in which the desired information is entered....

"What else are you doing, friend? How are your camphor compounds? Keep on working, friend!

"Devotedly and sincerely yours,

.N.Zinin."

The minutes of the meeting of the Physico-Mathematical Section of the Academy of Sciences of December 16th in that same year 1853 read: "Par. 308: Academician Fritzsche submitted a note on behalf of Prof. Butlerov of Kazan, entitled: 'Ueber das Oel des Pulegium micranthum (Claus)', and a note by Prof. Zinin, 'Ueber die Quisamensaure'. These papers will be published in the Bulletin." (Cf Minutes of the sessions of the Physico-Mathametical Section, December 16, 1853, Pars. 308, 309.)

A student of A.M.Butlerov's in the Faculty of Physics and Mathematics of the University of Kazan and an honorary academician, P.D.Boborykin,* the writer, was also interested in whether Butlerov's dissertation had been printed.

In a collection of unpublished letters from Boborykin to Butlerov, preserved in the Archives of the Academy of Sciences, there is a letter from Boborykin dated Dorpat, February 8, in which he writes to Butlerov:

"I wanted to ask you a long time ago: is your doctoral dissertation in print? I should like to look through it. There are few Russian books in the local library,

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*The writer P. D Boborykin was a student in the Faculty of Physics and Mathematics of the University of Kazan and studied chemistry under A. M. Butlerov. He translated Leman's Chemistry from the German. Concerning A. M. Butlerov, cf. P. D. Boborykin. Half a Century. (My Recollections). Moscow-Leningrad (1929), pp. 75, 84-86.

and still fewer dissertations."*

Thus, none of the contemporaries of Butlerov were able to acquaint themselves with his dissertation, which is why all the researchers and specialists on Butlerov's scientific work, not knowing the contents of the dissertation, limit themselves to mentioning it.

It is possible that Butlerov himself thought it undesirable to print the dissertation as a whole, but printed only its experimental section in the Bulletins of the Academy of Sciences, which A.M.Zaitsev rightly pointed out, as cited above.**

The copy of A.M.Butlerov's doctoral dissertation preserved in the library of the Polytechnic Institute contains 116 lithographed pages on 58 sheets.

It is worthy of note that the first page of the dissertation bears autographs - the signatures of members of the Council of the University of Moscow who had read the dissertation. They include the signatures of A.St.Yershov, A.Davydov, N.Zernov, the signature of the dean of the Faculty of Physics and Mathematics, A.Fisher, and others and the notation: "Rec[eived] 16 Jan., 1854." Thus, this copy of the dissertation is an original - a document of considerable interest for the history of the Faculty of Physics and Mathematics of the University of Moscow as well.

A.M.Butlerov's doctoral dissertation, "Essential Oils," contains a historical description of the problem of the nature and classification of essential oils, an experimental investigation of the essential oil in the plant Pulegium micranthum (Claus), and a classification of essential oils with some of Butlerov's changes.

The doctoral dissertation enables us to judge the views of the young Butlerov before he propounded the theory of structure; it is a valuable document for understanding the sources of the opinions he developed later on.

The whole of the dissertation is divided into a series of paragraphs (41 paragraphs in all); it consists of the following sub-sections:

Historical

I. The Series of Hydrocarbon Essential Oils

1. The action of free oxygen upon the terebenes.***
2. The action of water upon the terebenes.
3. The action of hydrohalic acids upon the terebenes.
4. The action of halogens upon the terebenes.
5. The action of nitric acid and other oxidizing substances upon the terebenes.

II. The Series of Essential Oils That Contain Oxygen

The group of oils with a $C_{10}H_8$**** hydrocarbon member and substances related to them

A. The division of essential oils with the composition $C_{10}H_8O$.

B. The division of volatile oils with the composition $C_{10}H_9O$ or $C_{10}H_{10}O$.

The second group of oxygen essential oils that do not contain $C_{10}H_8$ or $C_{10}H_9$.

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*Archives of the USSR Academy of Sciences in Leningrad, Collection 22, Catalog 2, No. 28.

**The papers in the Bulletins of the Academy of Sciences are an almost literal transcription of the experimental section of the dissertation. (T.V.).

***Butlerov used the term "terebenes" instead of "terpenes".

****According to present-day terminology, we should write $C_{10}H_{16}$ instead of $C_{10}H_8$ and $C_{10}H_{16}O$ instead of $C_{10}H_8O$, etc.

Butlerov begins his dissertation with the following words:

"Organic chemistry, enriched by a multiplicity of the latest researches, already provides methods of systematizing a large part of the substances investigated by it. Moreover, in some instances, theory has guided experiment; in others, we possess enough observations to arrive at theoretical conclusions regarding the chemical composition of certain groups. Here my fellow-champions of science have a wide field for their future labors, which must result in filling the gaps and in generalizing our theoretical views still further. Because of this insufficiency of observations on certain groups, they are, as it were, isolated from the rest of the systematic body of the science, and do not constitute a complete whole. They still include, unfortunately, the interesting group of the essential oils."

He says elsewhere. "We understand by this name substances that are encountered for the most part in the vegetable kingdom and possess certain common properties: oiliness, volatility, a characteristic and usually strong odor, and inflammability. What is more, many of them have sharply different chemical properties, and if we use purely chemical characteristics as the basis of classification when we make a closer study of them, as has been done in other instances, we find that they group of essential oils must be subdivided still further. By now some of the members of this group have been assigned their rational place and have been recognized as substances containing a radical. Many of the essential oils, in the form in which they are "prepared by vegetable organisms," constitute mixtures of substances of differing chemical composition, and if chemistry is compelled to accept the current classification, it is solely because of the insufficiency of research."

Butlerov repeatedly comments in his dissertation upon the inadequate research that has been done on the essential oils and writes:

"Since organic chemistry has become an independent science, many essential oils have been subjected to accurate analysis to determine their constitution and their contents; but we still have not made much progress along that road. The number of substances belonging to the class of the essential oils is increasing uninterruptedly with the extraction of new ones, and how insignificant is the number of those known to us that have been thoroughly investigated from the chemical standpoint, while the closest study of them is all the more important since we encounter the greatest diversity here." (Par. 6).

Starting with the data in the literature, Butlerov draws a series of basic conclusions regarding the essential oils. He establishes, first, the complexity of this class of substances, their instability, and the readiness with which they can change, and second, their identity or their isomerism.

As is seen from the subdivisions of the dissertation, Butlerov classifies the essential oils according to their composition, including in the first group the essential oils that contain the hydrocarbon $C_{10}H_8$. The second group contains oxygen as well as carbon and hydrogen; he divides this second group according to the ammount of oxygen it contains. Butlerov calls our attention to this circumstance particularly. Thus, in Par. 7, he states:

"The presence or absence of oxygen has an important influence upon the chemical nature of essential oils, so that, for lack of a better basis of classification up to the present time, we must adopt a division of essential oils into two series: the hydrocarbons - the camphenes (the terebenes of Liebig) and the oxygen essential oils. The first series is quite natural: the substances in this group have much in common as far as their chemical nature is concerned; whereas the second series must be subdivided still further, owing to the diversity of the properties of the substances therein." (Par. 7).

He then cites as an example of a "special subdivision of the second series" the common (laurel) camphor $C_{10}H_8$ and the essential oil he had investigated in Pulegium micranthum (Claus) and adds (Par. 7):

"Common (laurel) camphor $C_{10}H_8O$ belongs to the first group as far as the numerical ratio of the equivalents of carbon to those of hydrogen are concerned, whereas its containing oxygen places it in the second group. At the same time, it may be synthesized from bornene, which is a true camphene, by converting the latter into bornenic acid and then, by means of nitric acid, into laurel camphor. Thus, this camphor and some substances that are isomeric to it, such as the oil of Pulegium deserticola (Claus) that I have investigated, the oil Menthae Pulegii, and caryophyllin, will constitute transitional members, connecting one series of essential oils with the other, and may themselves constitute an intermediate group or, as we have done here, a special section in the second series, containing all the oxygen essential oils. Not having a better basis for subdividing this series, we take the hydrocarbon portion of their constitution as the distinguishing factor. The essential oils that contain a radical have, as has been noted above, already found their rational place in chemical classification and are not included in our description."

Commenting on the difficulty of their study and on the small quantity of experimental research on the terpenes, Butlerov remarks:

"We still haven't enough research results to be able to decide whether the compounds are identical or merely isomers. The ease with which the terbenes change into isomeric substances is a special handicap for the chemist in this case" (Par. 12).

The isomerism problem interested Butlerov intensely, and he sets up a number of propositions:

"It would be interesting to know," he writes in Par. 14 of his dissertation, "whether some of the oils recovered from the hydrochlorides by means of lime are not the same as those recovered by means of P_2O_5 from the hydrates of turpentine. It would be no less remarkable to learn the degree to which the number of isomeric $C_{10}H_8$ oils could be multiplied by treatment with hydrochloric acid, recovery with lime, a retreatment of the product by the same method, etc. Would the oil finally turn into something unchangeable (say, terebene, possibly), or changing, would it yield a series of isomeric substances, the properties of which would point to certain laws? Aren't two series of isomeric substances formed here: one reacting to polarized light, and the other inactive, like the changes of tartaric and malic acids, which Pasteur has described recently?"

Toward the end of the dissertation he returns to this analogy and, referring to Par. 8, writes:

"In Par. 8 I said that it would be highly advantageous to trace the transitions of the terebenes into isomeric substances, with the resulting changes in their behavior toward polarized light. The interesting and important discovery by Pasteur (Compt. rend. 37, p 162; Chem.Pharm Zentralblatt, No. 39, 1853), who has found three different tartaric acids and has demonstrated their relationship to racemic acid, already points the way, in part, to the standpoint from which we can probably consider the differences in the behavior of the terebenes to polarized light."

Here Butlerov poses the extremely interesting problem of the existence of optical racemic ("inactive") forms of the terpenes, by analogy with Pasteur's experiments on tartaric acid, and applies the latter's conclusions to the terpenes. This is particularly remarkable because Butlerov had not yet formulated his theory of structure,* and he was posing these questions as a forecast of new theories based

*This is Ariadne's guiding thread in organic chemistry (as A. E. Arbuzov has put it.)

upon new experimental researches. Butlerov adds:

"In general, terbenes "prepared by nature" are converted with extraordinary ease into new isomeric substances when acted upon by certain reagents; this involves a change in their behavior toward polarized light. It would be highly profitable to trace these conversions that take place without any change in composition in detail. But, unfortunately, we do not possess an abundance of observations in this field." (Par. 8)."

Pointing out how little we know of the part played by essential oils in the "economy of the vegetable kingdom", Butlerov expresses the very significant notion that the quantity of an essential oil in a plant varies in accordance with external factors. He writes:

"Since organic chemistry has become an independent science, many essential oils have been subjected to accurate analysis to determine their constitution and their contents; but we still have not made much progress along that road. The number of substances belonging to the class of the essential oils is increasing uninterruptedly with the extraction of new ones, and how insignificant is the number of those known to us that have been thoroughly investigated from the chemical standpoint, while the closest study of them is all the more important since we encounter the greatest diversity here. We know even less of the part played by the essential oil in the economy of the vegetable kingdom. To judge from the fact that some of them are deposited within the plant, we cannot but hazard the guess that this is of especial importance in the organic process. It is often the case that different parts of the same plants contain different essential oils. The quantity of oil varies in each specimen, depending upon the age, the soil, and particularly upon the climatic conditions." (Par. 6).

This concept of Butlerov's, which he was the first to enunciate in the science, was subsequently developed in the researches of Soviet scientists and chemists.

Turning then to a new essential oil from the plant Pulegium deserticola (Claus), on which no research had hitherto been done, Butlerov points out the singularity of its chemical properties and uses it as an example of a transitional group of compounds in the classification system referred to above. Butlerov isolated a substance with the composition $C_{10}H_{16}O$ from the essential oil of this plant, which proved to be isomeric with camphor. The experimental portion of the dissertation is devoted to a description of the properties of this camphorlike substance and to the numerous transformations it can enter into.

"Isomerism - the existence of compounds of identical composition and molecular weight, but with different properties - was explained most strikingly by the theory of structure, which made it possible to predict how many isomers might be expected for a given composition and molecular weight. Butlerov's theory of structure shed light upon the isomerism of hydrocarbons, indicated new possible instances of of isomerism among them, and determined the number of such possible cases. This explanation of isomerism in hydrocarbons led to the study of these phenomena in other types of organic compounds.

Butlerov was the first to prepare isobutane, the isomer of butane C_4H_{10}, as well as isobutylene. At the present time, di-isobutylene is employed in an addition reaction to produce iso-octane, a hydrocarbon that is used to determine the quality of gasoline (its "octane number").

Thus Butlerov's work has been of great practical value, in addition to its theoretical importance.

At the present time the isomerism of several terpenes has been studied, and in the subsequent work of Russian chemists - the outstanding researchers on the terpenes - the problems posed by Butlerov have been brilliantly resolved.

In his characterization of its properties, Butlerov writes:

Par. 25. "The plant discovered by Professor Claus in the southern steppes along the Volga, which he has named Pulegium deserticola, contains a special essential oil, the chemical composition of which is quite remarkable. In the crude state this oil is light yellow, with a taste that is hot at first and then cool, and it burns with a bright flame, evolving soot. Its odor, which resembles that of the oil of curly mint, Ol. menthae crispae, also reminds one of the odor of peppermint and sage. Nothing is recovered by cooling it to 17°C. When distilled, it begins to boil at 202°C; but then the thermometer rises gradually to 227°, whereupon the oil distils rapidly; the contents of the retort slowly acquire a brownish-yellow color. We may infer from this that the oil Pulegii deserticola is not a mixture of various substances or these substances have almost identical boiling points. The rise in the boiling point is due to the constant thickening of the residue as the result of its tar content, formed by exposure to the air. The distilled oil is quite transparent, nearly colorless, just a bit yellowish. Its specific gravity at 15°C, derived by me from two observations that differed but slightly, = 0.932."

Butlerov then makes an elementary analysis of the freshly distilled oil, the accurate numerical data he secured corresponding to a molecular formula of $C_{10}H_{18}O$ (Par. 25).

Butlerov was the first to obtain the ketone pulegone in the pure state. He subjected this substance to numerous reagents: atmospheric oxygen, anhydrous phosphoric acid, chromic acid mixture, fuming nitric acid, and strong solutions of caustic potash. The reaction with chromic acid mixture yielded products of deep decomposition, "meth-acetonic" and acetic acids.

It is remarkable that in his doctoral dissertation, Butlerov outlined a series of problems in the chemistry of the essential oils and the terpenes, and that after a long scientific career, devoted to the resolution of problems of the structure of organic compounds, he should have returned, 32 years later, at the end of his life, to this topic that interested him so much. Butlerov's last paper dealt with asarone (asarum camphor* [8]) and its structure.

In all probability, his interest in this series of organic substances had not died out, but had merely been "blocked" by other important problems, and only after having solved these latter could Butlerov, toward the close of his life, return to the research on one of the organic compounds encountered in the essential oils.

His paper on asarone (Part II) was read by A.I.Gorbov at the meeting of the Russian Physico-Chemical Society on September 11, 1886 [7], one month after Butlerov's death.

Russian chemists have played an outstanding part in the study of the chemistry of the terpenes. The growth of any branch of chemistry is closely associated with the development of new methods of research. Such a role in the study of the terpenes was played by the method developed by the prominent nineteenth-century Russian chemist E.E.Vagner, who proposed to oxidize the terpenes with a weak solution of potassium permanganate.

In addition to E.E.Vagner, the outstanding Russian chemists F.Flavitsky, L. Chugayev, I.Kondakov, and M.Konovalov, did considerable work on the chemistry of the terpenes. The classic researches of A. Reformatsky and V.Markovnikov on rose oil and the researches of P. Golubev on pine oil are well known.

The deeper penetration of this extremely interesting and difficult branch of chemistry is linked with the names of celebrated Soviet chemists: S.S.Nametkin,

*In his dissertation Butlerov refers to the properties of asarone (Par. 40).

A.E.Favorsky, Demyanov, P.D.Zelinsky, as well as B.A.Arbuzov, G.V.Pigulevsky, F. Tserevitinov, and others. In recent years the link between terpene chemistry and newly born fields of chemistry has been explored: with the chemistry of the polyterpenes and with plant pigments and vitamins.

Lastly, the development of the chemistry of the sterols and hormones owes much to the experience gathered in the study of the terpenes and polyterpenes. The problems of the essential oils and the compounds of the terpene group: turpentine, camphor, and rubber, have become important economically.

In the USSR new branches of industry have been established that did not exist in old capitalist Russia.

These industries include the production of natural and synthetic perfumes.

Czarist Russia did not possess the abundant fields of odoriferous plants, required for the food, pharmaceutical, soap, and perfumery industries. The variety of cultivated plants was extremely limited.

Today the picture has changed markedly. Plantations of scented plants have been established that can meet the needs of industry. New plants are being acclimatized on a large scale.

The work of selection and breeding performed by Soviet scientists has disclosed a number of valuable properties of plants (high oil content, quality of the oil, etc.).

The extensive work done in studying the wild flora of the USSR, which were wholly ignored formerly, has made it possible to find substitutes that grow in our country for many tropical plants used in industry (dragon's head, etc.). Technically equipped essential oil plants have been established in the Soviet Union for processing odoriferous plants. Considerable work has been done, and is being done, on the synthesis of odoriferous substances.

A broad field of activity lies before Soviet chemists in the synthesis of volatile odoriferous substances, making use of the rich flora of the USSR and resolving the problems that were merely guessed at and outlined in the work of the leading figures of Russian science, one of which is the doctoral dissertation of a founder of Russian chemical science – Alexander Mikhailovich Butlerov.

LITERATURE CITED

[1] N.A.Menshutkin, J. Russ. Phys. Chem. Soc., 19, 6 (1887).

[2] A.M.Zaitsev, J.Russ. Phys. Chem. Soc., 19, 23 (1887).

[3] A.P.Borodin and A.M.Butlerov, J. Russ. Phys. Chem. Soc., 12, 3, 221 (1880).

[4] A.Butlerov, Bull. de la classe Physico-mathematic de l'Academie des Sciences, XII, 16, 241 (1854).

[5] A.M.Zaitsev, J. Russ. Phys. Chem. Soc. 19, 23 (1887).

[6] B.Rizza and A.Butlerov, J. Russ. Phys. Chem. Soc. 16, 561 (1884).

[7] J.Russ. Phys. Chem. Soc. 19, 1, 16, (1887).

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THE INCRUSTATION OF SODIUM SULFATE UPON A HEATING SURFACE WHEN CHEMICALLY ACTIVE REAGENTS ARE PRESENT

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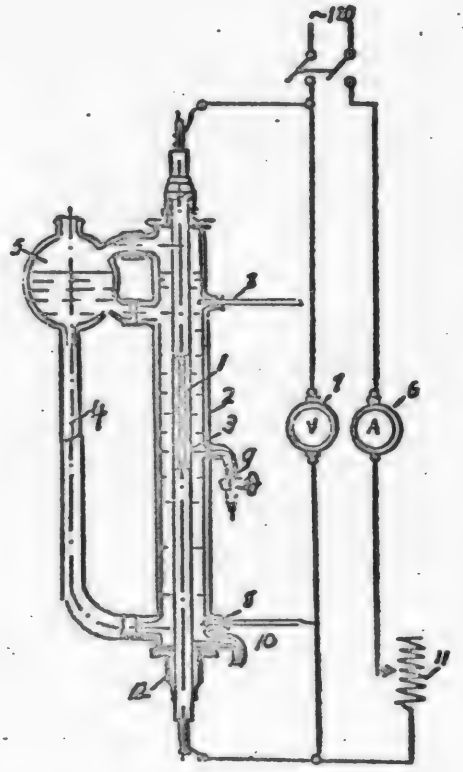
The permanent deposition of salts upon heat-transfer surfaces is a serious handicap in carrying out numerous technological processes involving the mass recovery of salts from solutions: evaporation, crystallization, etc. In some instances these difficulties constitute an insurmountable obstacle to the design of continuous-process equipment.

And yet, the scientific and technical literature contains almost no reference to experimental research on this phenomenon. The recently published research by Styrikovich and Kazakova [1] on the feasibility of sulfate incrustation is a paper whose topic comes close to the problem we have posed. In their research the heating surface was the surface of a platinum wire, heated by a current passing through it and plunged into a sulfate solution in order to produce local boiling. The authors found that no sulfate was deposited on the surface of the wire when an unsaturated solution of the sulfate was brought to a boil; only when they shifted to tests with a solution of another salt - gypsum - with its specific properties, did they discover any deposition of the salt on the wire when an unsaturated solution was brought to a boil. Thus, even in this paper, the phenomenon of incrustation proper was not the specific topic under consideration, and the limits of saturation concentration were not reached for even one salt: sodium sulfate.

Sodium sulfate, which is often met with in chemical industry, can settle permanently - be incrusted - upon surfaces used to heat its solutions. We were therefore particularly interested in it, as this example might shed light upon the fundamental chemical factors affecting that phenomenon. The present research was undertaken with that objective in mind.

The laboratory equipment (diagram) consisted of vertical steel tube (1) with an outside diameter of 16 mm, and an effective height of 600 mm. The tube was mounted by means of solid flanges, inside a glass housing (2) with an inside diameter of 70 mm. The tube was heated on the inside by an electric coil. The test

solution was contained in the cylindrical space between the tube and the housing. In the tests using a boiling solution, the latter circulated from the foregoing cylindrical space to the steam separator (5) and the return tube (4) to prevent emulsification of the solution by steam bubbles. Additional solution required to make up for evaporation, as well as added reagents, were introduced into the solution via the steam separator (5).



Cross-section of the laboratory apparatus for studying incrustation.

1-Steel tube 2-glass housing; 3-electric heating coil 4-circulating tube; 5-steam separator, 6-ammeter 7-voltmeter; 8-thermometer; 9-stopcock for taking samples; 10-drain tube, 11-rheostat 12-rubber bushing.

The first experiments were run with aqueous solutions of chemically pure sodium sulfate.

The solution, saturated at 40°C, was heated to 60-90°C. According to the solubility curve, this ought to cause a large quantity of anhydrous sulfate to settle out. This settling out actually took place throughout the solution, both under rapid and slow heating (up to 5 hours). The precipitated sulfate caused no incrustation; it did not settle on the heated walls of the steel tube.

The weak sulfate solution, 100-150 g per liter, was boiled in the apparatus for 6 to 8 hours, with fresh solution constantly being added as evaporation progressed. The rate of evaporation was about 20 to 30 kg of water per hour per m^2 of heating surface, which is about the usual value for evaporating apparatus. During evaporation, large quantities of the sulfate were precipitated out of the solution. But no incrustation of this precipitating sulfate on the heating surface was observed in this case either.

These results clearly contradict the generally accepted industrial estimate of sulfate as a salt that forms incrustations readily. The difference in behavior of sulfate in our case and in production equipment may well be due principally to the more complex composition of industrial solutions. First of all, industrial solutions are rarely exactly neutral; that is why we tested the effect of acidity and alkalinity of sulfate solutions upon incrustation. These tests on heating and boiling the solutions were run exactly as before, with sulfuric acid or caustic soda added to the solution during the process of heating or boiling.

The tests indicated that the presence of free acid had a great effect upon the

formation of a crust. Both at high additions of acid: up to 2.0 g H_2SO_4 per liter of solution, which even caused vigorous evolution of hydrogen : the corroded steel, and at low percentages - down to 0.1 g of H_2SO_4 per liter of solution, all the surface of the steel tube was covered with a dense layer of sulfate crystals as soon as the salt began to settle out of the evaporating solution.

The addition of caustic soda caused no incrustation. When the excess alkalinity was 0.1 g per liter, the heating surface remained completely clean both during heating and during boiling of the sulfate solution.

Moreover, in this series of experiments we tested the effect of introducing a strong oxidizing agent - sodium bichromate. The result was exactly the same as when sulfuric acid was added: the heating surface of the steel tube was soon covered with a dense layer of sulfate crystals. Assuming that the sodium bichromate may act as an acid salt, rather than as an oxidant, we then tried the addition of a neutral oxidant, sodium monochromate. The same result was obtained, however: the entire heating surface was soon covered with a permanent layer of crystals, even when only 1 g of the sodium monochromate was added per liter of solution. To complete the comparison, we then tested the addition of a reducing agent - sodium sulfite. As might have been supposed, the presence of the reducing agent did not cause any incrustation during the heating or boiling of these solutions.

To confirm the effectiveness of reducing the oxidants in the solution in order to prevent incrustation, we effected the preliminary reduction of the bichromate by adding the sulfite to a solution of the bichromate mixed with the sulfate. After this solution had been boiled to reduce the bichromate completely and after the precipitates of trivalent chromium compounds had been eliminated, the solution was heated and boiled, but no incrustation took place.

Finally, we tested the feasibility of nullifying the activity of the oxidizing agent: sodium monochlormate, by setting up free alkalinity in the solution. In fact, when the solution contained 1.0 g of the monochromate per liter, which produced heavy incrustation of sulfate on the surface in a neutral solution, this incrustation was prevented by having 0.05 g of caustic soda present per liter of solution.

It was natural to assume that the active effect of an acid or an oxidant upon incrustation is due to a change in the composition and structure of the heating surface, i.e., the outside of the steel tube. To clear up this question we ran tests in which the heating surface received a preliminary treatment: subjecting it to the action of aqueous solutions of the same sulfuric acid, bichromate, and monochromate.

After this treatment, the heating surface within the cylindrical operating space in the apparatus was washed 2 or 3 times with water, the sulfate solution was poured into this space, and the tests involving the heating and boiling of this solution were resumed.

The results of these tests exhibited a complete absence of incrustation.

Hence, we had to conclude that what was important for incrustation was not the end result of one change or another in the composition and structure of the heating surface when exposed to the action of these chemical reagents, but rather the fact that this action takes place simultaneously with the precipitation of salt crystals upon the surface.

Disclosure of the precise mechanism of such a combined process of chemical reaction and salt incrustation at a surface requires a profound study of the phenomenon in question. We are, however, justified by now in asserting that the formation of

new chemical compounds at the heating surface, during the very process of formation, establishes particularly favorable conditions for the activation of adsorption phenomena, evident in the preceding incrustations, and for the possible production of intermediate crystallizing layers binding the surface of the metal to the crystals of the deposited salt.

The incrustation of salts on the working surfaces of equipment is manifested in an extraordinary variety of conditions and ways. Some salts possess the marked ability to form permanent incrustations, while others, less common, exhibit absolutely no incrustation over a wide range of operating conditions.

The composition and structure of the precipitation surface has a definite effect upon incrustation phenomena. But, as our preliminary tests have shown, there is no correspondence between the crystalline structure of the metal surface and the crystalline structure of the incrustating salt, as might have been assumed theoretically. Moreover, solid incrustations of salts take place upon obviously non-crystalline materials: wood, bakelite, rubber, etc. The purely external characteristics of the surface are very important: a smooth surface, without projections, depressions, or cracks, especially a polished surface, will always exhibit less incrustation than an uneven surface. This smoothness and density of a surface is probably also responsible for the greatly reduced tendency of salts to form incrustations on glass or enamel surfaces.

Lastly, as a process that comes under the heading of surface phenomena, incrustation doubtless depends upon the presence of surface-active substances in the solution, especially upon surface-active colloids of an inorganic or organic nature.

All these varied factors responsible for the phenomenon of incrustation, together with the purely technical, design, and operating conditions under which the various technological processes are carried out, require an extensive and profound study of the phenomenon in question. But even the facts on the initial stages of this research cited in the present brief report: the influence of the basic chemical properties of the medium (the solution) upon the incrustation of a specific salt (a sulfate) are of some scientific and technical interest.

In all cases where the solutions containing a sulfate are somewhat acid or contain a minute amount of an oxidizing agent, it may be possible to neutralize this acidity or to reduce the oxidant by adding small quantities of some cheap reagents, thus facilitating the subsequent processing of these solutions by preventing the appearance of incrustation.

We have reason to believe that this manner of affecting the acidity, alkalinity, or oxidizing agents to influence the phenomenon of incrustation must exist in a large number of other mineral salts and may be employed there very effectively. In many instances the processing of salts involves processes of evaporation and crystallization, i.e., operations in which incrustation affects the operation of the equipment most seriously, and in which excess acidity and alkalinity and the oxidizing agents are usually present in small quantities. Neutralizing and reducing these solutions require small expenditures for the alkalies and deoxidizers that have to be added, which are fully justified by the elimination of the complications introduced by incrustation phenomena.

SUMMARY

1. It has been found that sulfate incrustation on a heating surface depends markedly upon the basic chemical characteristics of the solution: acidity, alkalinity, and the presence of oxidizing agents.

Barium chloride and sodium chloride exhibit the same effects when their solutions are evaporated.

2. The absence of incrustation when the solution is neutral or alkaline and when no oxidant is present makes it possible to recommend the prior neutralization and deoxidation of sulfate solutions in order to prevent incrustation.

LITERATURE CITED

[1] M.A.Styrikovich and E.A.Kazakova, Doklady Akad. Nauk. USSR., 5 (1949).

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THE MICROSTRUCTURE OF ANHYDRITE CEMENT

I. Ya. Golosovker

Anhydrite cement was first proposed by Academician Budnikov (1920) [1]. It consists of anhydrite ($CaSO_4$), produced by roasting gypsum dihydrate ($CaSO_4 \cdot 2H_2O$) at a temperature of 600-700°, followed by grinding it to a fine powder together with various catalysts.

The presence of the catalysts facilitates the hydration and crystallization of the anhydrite. Inasmuch as anhydrite does not produce crystals within the observed periods (1 to 2 days) when no catalysts are employed, it may be assumed that what takes place is not the spontaneous, but rather the forced, starting of crystallization, due to the introduction of a primer (the catalyst).

Shubnikov [2,3] has voiced the supposition that the colloidal particles of the catalyst concentrate (adsorb) the molecules of the given substance upon their surface even in an unsaturated solution, thus establishing potential centers around which crystallization sets in when the solution becomes supersaturated.

Rubinshtein [4] also assumes that the presence of a catalyst promotes rapid crystallization.

According to the modern theories of catalysis, the primary crystalline formations, i.e., the elementary minute crystals of the catalyst, are the carriers of this activity.

We had as our objective a study of the process of crystallization of hydrated anhydrite with various catalysts by means of microscopic observation.

Inasmuch as the tiniest crystals of the crystallizing substance itself may serve as the primer, we made our observations on hydrated anhydrite to which finely pulverized crude gypsum dihydrate had been added as a primer.

EXPERIMENTAL

A solution of anhydrite, the catalyst, and water was gotten up in order to produce the preparations required. The catalyst constituted 2% by weight of the anhydrite. The water constituted 55% by weight of the cement. When a complex catalyst, consisting of two substances, was used, each of them constituted 1% of the

anhydrite, by weight. To ensure its even distribution throughout the solution, an accurately weighed batch of the catalyst was dissolved in the water, and the anhydrite was added to this aqueous solution. After the solution had been carefully stirred with a glass rod, it was transferred to the object glass.

The preparation was not covered with a cover glass; it was kept in an exsiccator above water for 1 to 2 days. Keeping the preparation in the exsiccator without a cover glass ensures the optimum conditions for hydrating the anhydrite and does not distort the process of crystallization.

The procedure and storage times set forth above were employed for all the catalysts tested, with the exception of lime. The lime was added as slaked lime, [$Ca(OH)_2$], constituting 8% of the anhydrite by weight, and the preparation was kept in the exsiccator for 7-10 days.

A total of several thousand observations were made, plus three hundred microphotographs. Seven of the most typical photographs are appended to the present paper.

The results of our microscopic observations are shown in the subjoined table and in the microphotographs.

Crystallization of Hydrated Anhydrite

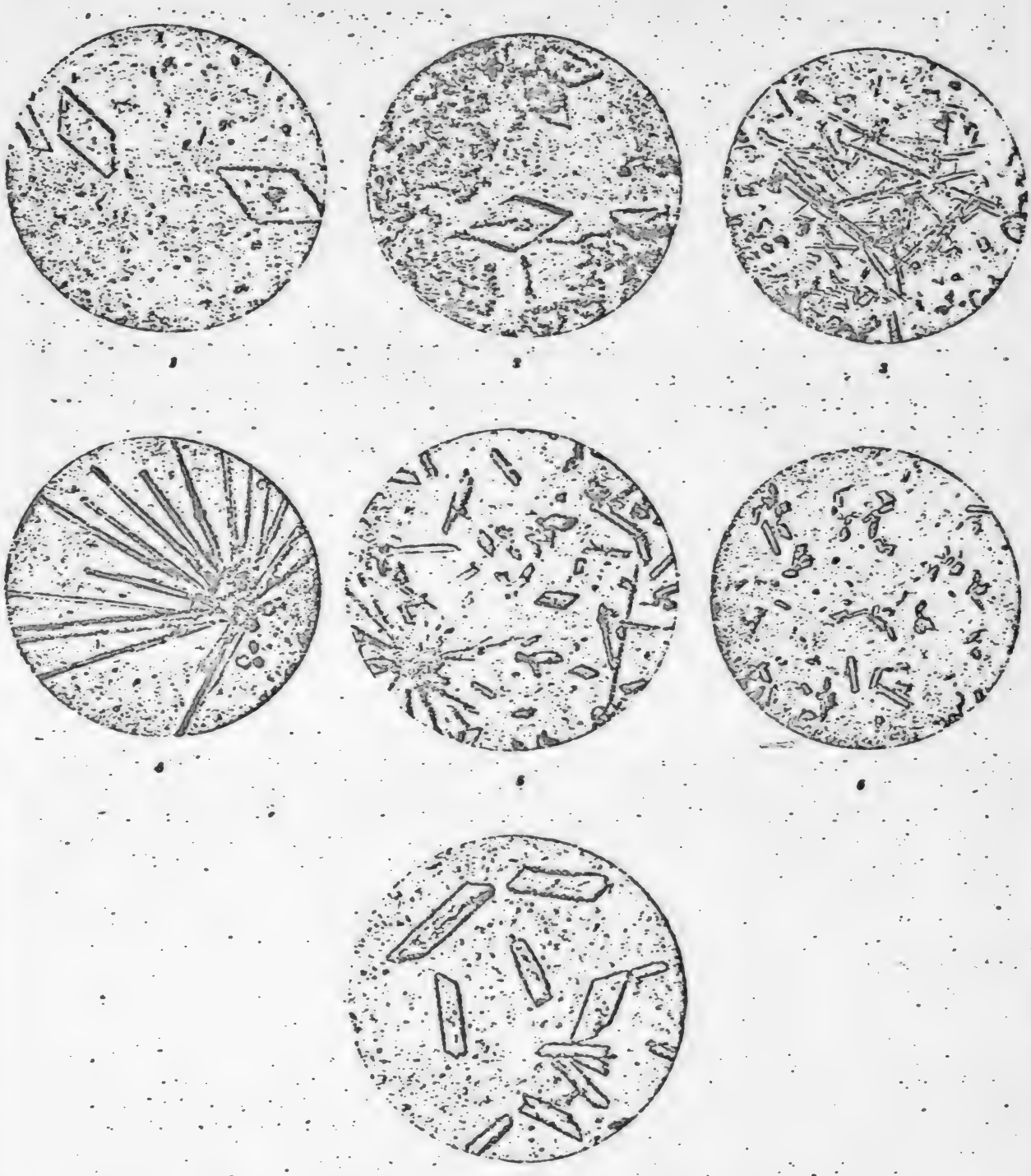
Catalyst	Kinds of crystals and peculiarities of crystallization					
	Acicular	Prismatic		Pinacoid plane like a parallelogram	Radiating formation	"Swallow-tail" twins
		Up to 30μ long	Elongated			
K_2SO_4.....	Predom.	–	Frequent	–	Predom.	–
$KHSO_4$.....	–	Frequent	Predom.	–	Frequent	–
$K{\cdot}Al(SO_4)_2{\cdot}12H_2O$.	–	Frequent	Predom.	–	Frequent	–
$K{\cdot}Cr(SO_4)_2{\cdot}12H_2O$.	–	Predom.	–	–	–	–
$FeSO_4{\cdot}7H_2O$.....	Rare	Frequent	Predom.	Frequent	Rare	–
$CuSO_4{\cdot}5H_2O$	–	Frequent	Predom.	Rare	Rare	–
$K_2SO_4 + FeSO_4$....	–	Rare	Predom.	–	–	–
$K_2SO_4 + CuSO_4$....	–	Rare	Predom.	–	–	–
$KHSO_4 + FeSO_4$....	–	Rare	Predom.	Frequent	Rare	–
$KHSO_4 + CuSO_4$....	–	Predom.	Predom.	–	Rare	–
$Na_2SO_4{\cdot}10H_2O$	–	–	–	Predom.	–	Frequent
$Ca(OH)_2$	–	–	–	Predom.	–	Frequent
$CaSO_4{\cdot}2H_2O$.....	–	–	–	Predom.	–	–
$NaHSO_4$.....	–	–	Predom.	Predom.	Frequent	–
$Na_2SO_4 + FeSO_4$...	–	Rare	Predom.	Predom	–	Rare
$Na_2SO_4 + CuSO_4$...	–	Rare	Predom.	Predom.	Frequent	Rare
$NaHSO_4 + FeSO_4$...	–	–	Predom.	Frequent	Frequent	–
$NaHSO_4 + CuSO_4$...	–	–	Predom	Frequent	Frequent	–

To make sure that the crystals formed with various catalysts used were actually gypsum dihydrate, we made the necessary observations in polarized light.

We determined the refractive indexes of several preparations by the immersion method and secured results that are characteristic for gypsum ($\alpha = 1.521$, $\gamma = 1.530$).

The interference color was found to be low in all instances (gray, dull-gray, grayish-yellow).

The extinction angles varied from 22 to 35°.



Microphotographs of crystals of hydrated bypsum when different catalysts are used.

1 – Na_2SO_4; 2 – Na_2SO_4; 3 – K_2SO_4; 4 – $K_2SO_4 + CuSO_4$;
5 – $FeSO_4$; 6 – $Na_2SO_4 + CuSO_4$, 7 – $K_2SO_4 + FeSO_4$.

The results of our optical observations in polarized light convinced us that we were looking at gypsum crystals in every instance.

SUMMARY

1. The setting and hardening process in anhydrite is related to its hydration and recrystallization.

The catalyst, apparently separating out of the solution in the form of minute crystals, establishes potential centers for the crystallization of hydrated gypsum.

2. Each catalyst is characterized by its own form of gypsum crystals, ranging from the acicular to crystals that are fairly large, whose pinacoid plane is a parallelogram.

Inasmuch as the formation of gypsum crystals takes place under identical conditions for the various catalysts (solution concentration, temperature, hydration conditions), the formation of different kinds of crystals must depend upon the kind of catalyst employed.

3. The catalysts Na_2SO_4, $Ca(OH)_2$, and CaO, and the primer $CaSO_4 \cdot 2H_2O$ are characterized by a form of gypsum crystals that exhibits a marked monoclinic syngony with a pinacoid plane |010| in the form of a parallelogram. With these catalysts, prismatic or acicular crystals are not encountered as a rule (Figs. 1, 2).

4. Catalysts containing potassium [$KAl(SO_4)_2$, $KCr(SO_4)_2$, K_2SO_4, $KHSO_4$], are characterized by gypsum crystals of acicular and prismatic form, with the crystals interlaced and forming radial bundles (Figs. 3,4).

5. The catalysts $NHSO_4$, $CuSO_4$ and $FeSO_4$ are characterized by the presence of prismatic crystals, and by crystals with a pinacoid plane in the form of a parallelogram (Fig. 5).

6. When complex catalysts are used, the gypsum crystals, as a rule, have the forms that are characteristic of each of the catalysts separately (Fig. 6). But in some cases a complex catalyst imparts its own distinctive form to the crystals. K_2SO_4 + $FeSO_4$, for example, very often produce crystals shaped like elongated little prisms, with dimensions ranging up to 19 x 125 microns. Bent (sabre-shaped) crystals are often observed (Fig. 7).

7. When the progress of crystallization at one point in the preparation was observed for a long time, it was noticed that the process of crystallization is completed within 6-12 hours with catalysts that contain potassium (K_2SO_4, $KHSO_4$).

With Na_2SO_4 the process takes 2 to 10 days. With $Ca(OH)_2$ this process lasts 10 to 20 days. During the course of 15 days new crystals are seen to appear in the microcrystalline mass, while the previous ones continue to grow, many of them coalescing together.

8. It was noted that the time requred for crystallization increases as the gypsum roasting temperature is raised within the 600-750° range.

The probable explanation for this phenomenon is that at lower roasting temperatures a small amount of gypsum semihydrate remains, which is hydrated and crystallized much faster than the anhydrite. The resulting crystals of gypsum dihydrate act as a primer that accelerates the crystallization of the hydrated anhydrite.

9. The time required for crystallization with various catalysts can be related to the nature of the rise in the mechanical strength of the anhydrite cement:

Our observations have shown that the ultimate compression strength after one

week is 64% of that after one month when $Ca(OH)_2$, which causes the longest crystallization periods, is used as the catalyst. With the $Na_2SO_4 + FeSO_4$ catalyst, which shortens the process of crystallization, the ultimate strength after one week is 80% of the monthly value.

10. Further study of the processes of crystallization of hydrated anhydrite and of the ways in which they are related to the physical and mechanical properties of anhydrite cement will make possible better utilization of the properties of this binding material.

LITERATURE CITED

[1] P.P.Budnikov. Coll. Research Papers on Building Materials. Industrial Construction Press (1947).

[2] A.V.Shubinkov et al. Principles of Crystallography. USSR Acad. Sci. Press. (1940).

[3] A.V.Shubinkov. The Formation of Crystals, USSR Acad. Sci. Press (1947).

[4] Symposium on Methods of Studying Catalysts. USSR Acad. Sci. Press, (1948).

Received June 12, 1950.

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THE REDUCTION OF Na_2SO_4 IN SILICATE SYSTEMS

A G Repa and E P Danilchenko

Na_2SO_4 is usually employed in the manufacture of Na_2O or Na_2S, the Na_2SO_4 being reduced in a current of gas (CH_4, CO, or H_2), or heated to high temperatures in a mixture with solid carbon.

Budnikov [1] has investigated the reduction of Na_2SO_4 by coal, and has come to the conclusion that reduction sets in at a temperature in excess of 750° and depends upon the kind of coal used. According to Budnikov, CO does not reduce Na_2SO_4 at temperatures below 850°. He attributes the drop in the yield of Na_2S as the temperature is raised and the time of roasting the Na_2SO_4-Coal mixture is increased to a reaction between the Na_2SO_4 and the Na_2S in accordance with the following equation:

$$Na_2SO_4 + Na_2S = 4Na + 2SO_2. \qquad (1)$$

According to Budnikov, the reduction of Na_2SO_4 by coal takes place largely in the solid phase. The reduction of Na_2SO_4 by gaseous reducing agents has been investigated by Nekrich [2], and by Ilinsky, Tarasov, and Ginsburg [3], who attributed the reduction to the following reactions:

$$Na_2SO_4 + CH_4 = Na_2S + CO_2 + 2H_2O, \qquad (2)$$

$$Na_2SO_4 + 4CO = Na_2S + 4CO_2, \qquad (3)$$

$$Na_2SO_4 + 4H_2 = Na_2S + 4H_2O. \qquad (4)$$

Notwithstanding the apparent naturalness of this process, it is unable to explain a single one of the many singularities of gaseous reduction. We know that gaseous reduction is characterized by a certain induction period, which is exceptionally long in the case of CO. This was the basis for Budnikov's assertion that CO practically does not reduce Na_2SO_4 at all in the solid state, the reduction being due to the direct reaction of the Na_2SO_4 with the coal.

No research has ever been done on the kinetics of the reduction of Na_2SO_4-SiO_2 mixtures. The mechanism of the process is unclear, which is why the reactions for the reduction of Na_2SO_4 – SiO_2 mixtures by solid and gaseous reducing agents proposed by Tammann and Olsen [4] is still commonly accepted. Their suggested process involves the three following equations:

$$Na_2SO_4 + C = Na_2SO_3 + CO, \quad (5)$$

$$2Na_2SO_4 + C = 2Na_2SO_3 + CO_2, \quad (6)$$

$$Na_2SO_3 = Na_2O + SO_2. \quad (7)$$

The resultant Na_2O reacts with the SiO_2, forming sodium silicate.

The inadequacy of this series of equations is proved by the following well-known facts: 1) anhydrous Na_2SO_4 and C yield Na_2S, and not Na_2O, as their end product; 2) only traces of sulfur dioxide can be found during the process of reduction in the gaseous phase; and 3) when heated, Na_2SO_3 breaks down into a mixture of Na_2SO_4 and Na_2S, and not into Na_2O and SO_2.

Many years of operation of glass factories have demonstrated that about 6% of coal must be present in sulfate glass batches for all of the Na_2SO_4 to be converted into Na_2O, and that the corrections for ash and moisture in the coal and for its partial combustion happen to yield exactly the quantity of carbon calculated from Equation (5). If two mols of C are taken for each mol of Na_2SO_4, it is found in practice that the reducing agent is present in tremendous excess. This has always been cited as the major argument in support of the Tammann scheme for the reduction of Na_2SO_4 by solid carbon. We all know, however, that the quantity of reducing agent required depends upon the overall moisture in the batch and the methods used to melt it. The operating procedures of glass factories that manufacture glass from sulfate batches indicates that the amount of reducing agent added to the batches varies widely, between 4 and 12%, whereas the quantity of Na_2SO_4 in the batch remains the same.

Thus, there are many things that are unclear in the reduction of Na_2SO_4, and far from enough work has been done on the reduction of Na_2SO_4 when mixed with SiO_2. It has been the objective of the present research to shed light upon the processes involved in the reduction of pure Na_2SO_4, as well as of its mixtures with SiO_2.

EXPERIMENTAL

The reduction of Na_2SO_4 and of its mixtures with SiO_2 by solid carbon was investigated by taking continuous readings of the changes in the weight of the sample being heated (Fig. 1). The furnace was heated up to the requisite temperature, which was maintained within $\pm 5°$. 10.0 g of the mixture was placed in a standard 100-ml corundum crucible. The mixture in the crucible was 17 mm deep, and it was not packed down. Nichrome wire was wound around the crucible in the shape of a netting. The netting was attached to a long quartz hook, the other end of which was attached to a balance arm of an analytical balance. Weighing the crucible, as well as lifting it out of the furnace, was done as rapidly as possible, usually being completed in 10-15 seconds. This enabled us to avoid observable fluctuations in the furnace temperature. Moreover, the rate at which the Na_2SO_4 is reduced becomes very high once the initial induction period is past; we therefore had to employ "chilling" in order to measure the magnitude of the reaction rate correctly during this interval of time. This was done by placing the crucible in an exsiccator as soon as it had been lifted out of the furnace, and then forcing a powerful current of chilled nitrogen through the exsiccator from a tank. As a rule, the major loss in weight, corresponding to the maximum rate of reduction of the Na_2SO_4, occurred within 2-3 minutes, as is clearly shown by the subjoined graphs. That is why the "chilling" of the crucible's contents in a current of neutral gas was absolutely necessary. (Failure to take these precautions led Budnikov [1] to conclude that the reduction of Na_2SO_4 diminishes as the temperature is raised.) The mixture's loss of weight was measured on the scales with an accuracy of 0.01 g. After the contents of the

crucible had cooled, they were dissolved in water, and their percentage of Na_2SO_4 was determined by analysis.

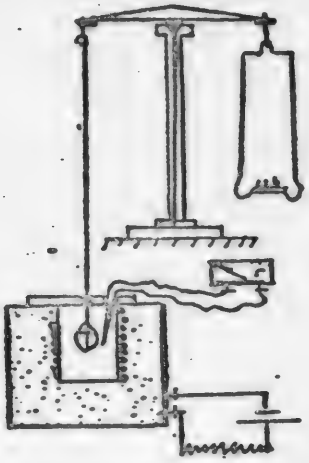

Fig. 1. Apparatus used for reducing Na_2SO_4.

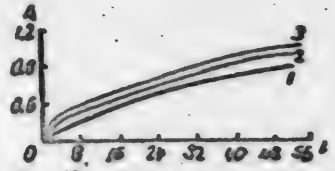

Fig. 2. Kinetics of coal combustion.

A-Mixture s loss in weight. g ;B-time. minutes.
1-Na_2SO_4 + 2C 650° 2-SiO_2 - 2C 900°
3-SiO_2 + 2C 1000°.

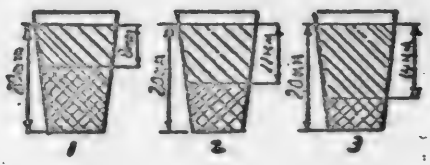

Fig. 3. Combustion of coal as a function of time. Temperature = 650°. Mixture composition: Na_2SO_4 + 2C.
Time in minutes: 1-60; 2-90; 3-120.

The reduction of mixtures of Na_2SO_4 + SiO_2 was investigated in currents of CO and H_2 with charcoal added to the mixture as a deoxidizer. The mixture of Na_2SO_4 + SiO_2 with charcoal added was placed in a corundum crucible and heated in the furnace as described above.

Cylindrical briquets were prepared in a press for the gaseous reduction of a (mol per mol) mixture of Na_2SO_4 + SiO_2. This was done by moistening the mixture and then pressing it under a pressure of as much as 15 kg per cm^2. The briquets, which weighed about 3 g, were desiccated in a thermostat at 100°. The initial binder used was fused mirabilite, which moistened the grains of SiO_2 and the tiny crystals of Na_2SO_4. The briquets exhibited high mechanical strength.

The briquet was placed in a platinum-wire basket and then lowered into the furnace. In this case the quartz hook was suspended from the end of glass scales. The change in weight was recorded continuously by means of a cathetometer. The gas was turned on after 20 minutes had elapsed and the briquet had reached the furnace temperature.

Reduction of Na_2SO_4 by coal. We used charcoal with an ash content of 1.02%. To improve comminution, we prepared 160 g of the charcoal, 10 g of which was taken for every single test.

The coal started to burn a few seconds after the test sample had been placed in the electric furnace; the higher the furnace temperature, the faster it burned. When a rapid loss of weight set in, drops of a melt began to form on the surface of the mixture. Repeated observations showed that the first drops of liquid appear at 720-725°.

The appearance of the liquid phase is related to the formation of a eutectic in

Na_2SO_4 + Na_2S system. The fusibility of this system was investigated quite carefully by Courtois [3] in 1939; earlier researches were marked by greater approximateness; this is particularly true of Tammann's results [4]. According to Courtois, the melting point of Na_2S is 1180 ± 10°, while the melting point of the eutectic, corresponding to 50% Na_2SO_4 + 50% Na_2S, is 730 ± 2°. The temperature of 720° observed by us is due to the contamination of the mixture with coal ash and, principally, to the partial hydrolysis of the Na_2S, which results in the formation of the low-melting NaOH.

The accumulation of Na_2S in the mixture raises its melting point; that is why the melt gradually solidifies at 740°, and the rate of reduction drops. The curve of the reduction of Na_2SO_4 takes on a very drawn-out shape.

As soon as the first drops of the melt appeared, the whole surface was covered with a caking crust, through which the gas passed with some difficulty. This evidently tends to speed up the reaction, since the rate at which the Na_2SO_4 is reduced is a maximum at this instant.

Up to 700° only coal burns out of the mixture, the surface of the mixture being covered with a pure white powder. At 700° the Na_2SO_4 turns slightly pinkish, indicating the onset of the reduction reaction.

The reduction of the Na_2SO_4 sets in at 700° and is independent of the kind of coal, provided two conditions are observed: 1) 2% Na_2S is added to the Na_2SO_4; and 2) up to 0.1% of gas tar is added to the coal as a source of volatiles.

The way in which the coal is burned out of the Na_2SO_4 + Coal mixture is shown in the graph in Fig. 2. The figure also gives the curves for the way in which the coal is burned out of a mixture of SiO_2 (sand) and coal at 900 and 1000°.

The burning-out curves have no induction period. The rate of combustion is clearly visible in Fig. 3, the burning out having been examined in transparent quartz crucibles. The results of these tests are listed in the subjoined table.

The data in the table were used to plot the graphs of "loss in weight vs. time" and "percentage of reduced Na_2SO_4 vs. time." It is characteristic that the maximum reduced Na_2SO_4 (Fig. 5) does not fully coincide with maximum loss in weight (Fig. 4). The

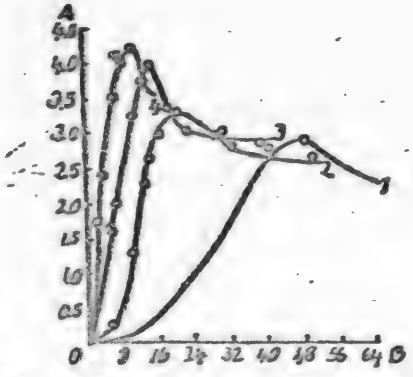

Fig. 4. Kinetics of loss in weight of a Na_2SO_4 + 2C mixture at various temperatures.

A-Percentage of reduced Na_2SO_4. B-time, min. Reduction temperature °C. 1-750 2-800 3-900 4-1000.

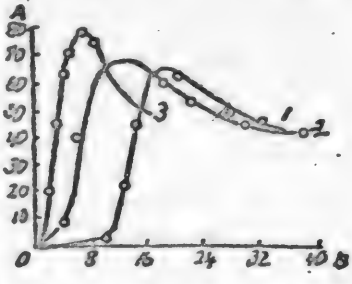

Fig. 5. Kinetics of the reduction of Na_2SO_4 by solid carbon at various temperatures.

A-Persentage of reduced Na_2SO_4; B- time, min. Reduction temp. °C. 1-800; 2-900; 3-1000.

$^1Na_2SO_4$

The difference is always 1.5-2 minutes at 1000, 900, or 800°. This is due to the impossibility of instantaneously "chilling" the reaction at the instant it attains maximum velocity, especially in the deeper layers of the mixture or the melt. The loss-in-weight graph indicates that the coal begins to burn away practically instantaneously, while the graph for the reduction of the Na_2SO_4 exhibits a certain induction period. The induction period grows shorter as the temperature is raised. It is typical that the curves have the same form for all kinds of carbon (carbon prepared from sugar, anthracite, brown coal), though the presence of volatiles in the coal always determines the following two phenomena:

1) The temperature at which the reduction reaction sets in is in the neighborhood of 700°;

2) The induction period is reduced to a minimum.

Loss in Weight of a Sample of Na_2SO_4 and Coal at Various Temperatures

Weight 10.0 g; Composition (in grams): Na_2SO_4 = 8.5542; Coal = 1.4458; Constituents Sifted Through a Screen With 900 Holes per Cm^2

Temperature (° C)												
650°		750		800			900			1000		
Time, (min.)	Loss in wt., g.	Time, (min.)	Loss in wt. g	Time, (min.)	Loss in wt. g	% Reduction of Na_2SO_4	Time, (min.)	Loss in wt. g	% Reduction of Na_2SO_4	Time, (min.)	Loss in wt. g	% Reduction of Na_2SO_4
10	0.32	10	0.41	6	0.54	-	4	1.49	9.90	2	1.72	-
20	0.49	20	0.76	8	1.08	-	5	1.60	-	2	1.76	20.70
40	0.65	40	2.65	10	1.30	3.13	6	2.00	41.20	3	2.41	46.10
60	0.88	40	2.69	12.5	2.20	24.00	9	3.02	-	4	3.54	64.10
80	0.99	48	2.87	14.0	2.64	45.10	10	3.22	67.00	5	3.20	70.91
100	1.05	60	2.40	16	3.01	62.83	14	3.32	68.02	6	3.47	70.90
120	1.14	70	2.12	20	3.34	63.03	18	3.36	60.00	7	4.17	79.12
-	-	-	-	28	2.91	51.15	22	3.08	51.70	8	3.92	75.63
-	-	-	-	32	2.78	47.32	30	3.01	46.12	9	4.20	-
-	-	-	-	50	2.60	-	38	2.83	43.00	10	4.16	61.00
-	-	-	-	-	-	-	-	-	-	12	3.75	-
-	-	-	-	-	-	-	-	-	-	14	3.62	52.5
-	-	-	-	-	-	-	-	-	-	16	3.55	49.8

Figures 4 and 5 exhibit a typical bend in the curves of the reduction of Na_2SO_4, indicating the presence of intensive oxidation of the Na_2S at the instant all the coal has been burnt away. Intensive "chilling" with cold nitrogen enables one to cut the oxidation of the Na_2S to 3 to 4 seconds.

The rate at which the Na_2S is oxidized decreases with time, as it is hampered by the diffusion of air within the melt.

Influence of the Carbon Concentration

The kinetics of the reduction of the following mixtures: 1) Na_2SO_4 + 3C, 2) Na_2SO_4 + 2C, 3) Na_2SO_4 + 1C, 4) Na_2SO_4 + 0.5C, at 750, 800, 900, and 1000 ° were investigated to shed light upon the effect of the concentration of carbon in the mixture upon the rate at which the Na_2SO_4 was reduced.

Figure 6 shows the curves of the loss in weight for the mixture containing Na_2SO_4 + 0.5 mol of C. We see that the reduction of Na_2SO_4 has merely set in at 740°. The mixture has merely begun to cake. The reaction is more clearly evident at 800°. The mixture is caking, but there is no liquid phase, which appears at 880° as the result of fusion of the Na_2SO_4. Thus, what happens is that the coal is burned out of the mixture; under the foregoing conditions the reducing effect is negligible.

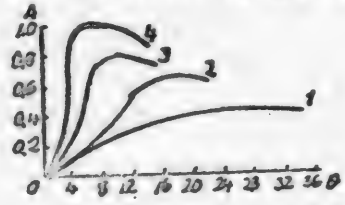

Fig. 6. Kinetics of the loss in weight of a Na_2SO_4 + 0.5C mixture at various temperatures.

A-Mixture's loss in weight grams B-time, min. Reduction temp °C. 1-740 2-800 3-900 4-1000.

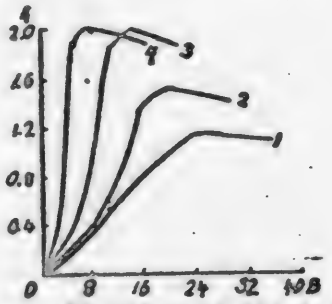

Fig. 7. Kinetics of the loss in weight of a Na_2SO_4 + 1C mixture at various temperatures.

A-Mixture's loss in wt. g.: B-time, min. Reduction temp. °C: 1-750; 2-800; 3-900; 4-1000.

Fig. 7 gives the curves showing the reduction kinetics for a mixture consisting of Na_2SO_4 + 1 mol of C. Here the deoxidizing effect is exactly twice as great as in the mixture containing 0.5 mol of C. The instant at which the reduction reaction sets in is clearly shown on the curves.

Figures 4 and 8 give the curves for mixtures consisting of Na_2SO_4 + 2 mols of C and Na_2SO_4 + 3 mols of C. We see that increasing the quantity of C to 2 mols doubles the effect once again, but that an increase in the quantity of C from 2 to 3 mols is less effective. This is due to the fact that the excess coal begins to burn at the very start, and the carbon concentration in the mixture drops.

The rate of reduction may be obtained by graphically differentiating the curves showing the kinetics of the reduction of Na_2SO_4. The drawings show that the rate depends considerably upon the temperature, and relatively little upon the concentration of carbon.

Fig. 9 shows the effect of the concentration of C upon the kinetics of the reduction of Na_2SO_4 at 1000°. The maximum loss of weight always lies on the straight line ab. The loss in weight remains proportional to the concentration of C only up to a carbon content of 2C. Further additions of C are less effective.

Reduction of Na_2SO_4 + SiO_2 Mixtures

Figure 10 gives the kinetics of reduction for mixtures of sodium sulfate with sand and charcoal. The shape of the curves is the same as in the previous graphs. But after the reduction of the Na_2SO_4 is complete, no gain in weight, which would reflect oxidation of the Na_2S, is observed. The higher the temperature, the higher the rate at which the Na_2SO_4 is deoxidized and the more it is deoxidized. Determination of the Na_2S formed gives a result that agrees with the quantity of Na_2SO_4 reduced.

The foregoing holds true only when the mixtures are carefully dried at 105°.

Fig. 8. Kinetics of the loss in weight of a Na_2SO_4 + 3C mixture at various temperatures.
A-Mixture's loss in wt., grams; B-time, min.
Temp. °C: 1-800; 2-900; 3-1000.

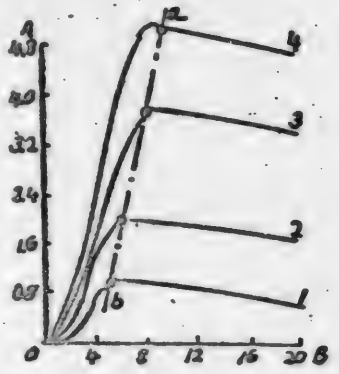

Fig. 9. Kinetics of the reduction of Na_2SO_4 as a function of the concentration of carbon in the mixture. Temperature 1000°.

A-loss in wt., grams; B-time, min.
Carbon content: 1-0.5C; 2-1C; 3-2C; 4-3C.

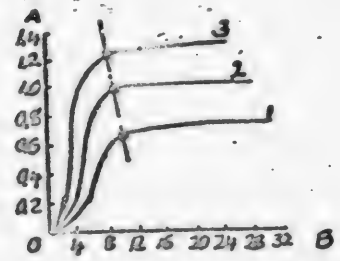

Fig. 10. Kinetics of the reduction of a Na_2SO_4 + $3SiO_2$ + C mixture at various temperatures.
A-Loss in wt., grams; B-time, min.
Temp. °C: 1-800; 2-900; 3-1000.

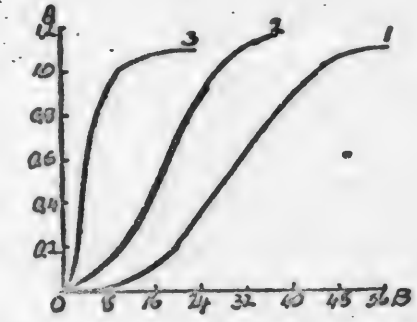

Fig. 11. Kinetics of the reduction of Na_2SO_4 + SiO_2 in a current of hydrogen. Rate of gas flow = 350 ml per min. Temperature 720°C.
A-Loss in wt., grams; B- time, min.
1- 33% H_2 and W_m = 0.31 g; 2-50% H_2 and W_m = 0.35 g; 3-33% F_2 and W_m = 1.65 g.

Otherwise H_2S and SO_2 are found in the gas phase, and sodium silicate accumulates in the mixture.

What is characteristic is the presence of a clearly marked induction period in these kinetics curves, which diminishes as the temperature is raised.

Figures 11 and 12 show curves for the reduction of briquets made of an equimolar mixture of Na_2SO_4 and SiO_2 at 720° in a current of hydrogen and carbon

monoxide, respectively. Deoxidation cannot be initiated at 720° in a current of CO. All of the briquet remains unchanged for the space of 2 hours in the CO current, though all we need to do is to have the carbon monoxide followed by a current of H_2 or illuminating gas for 20 to 30 seconds for the reduction of the Na_2SO_4 to commence and to continue smoothly. The hydrogen and the carbon monoxide were diluted with nitrogen.

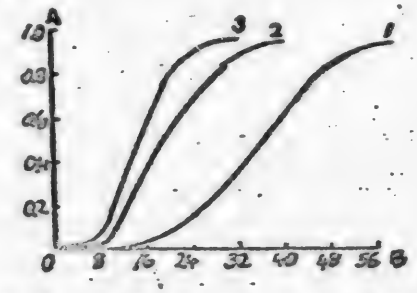

Fig. 12. Kinetics of the reduction of $Na_2SO_4 + SiO_2$ in a current of carbon monoxide. Rate of gas flow = 350 ml per min. Temperature 720°C.

A-Loss in wt., grams; B-time, min. 1-33% CO and W_g = 0.3g; 2-50% CO and W_g = 0.4g; 3-100% CO and W_g = 0.6g.

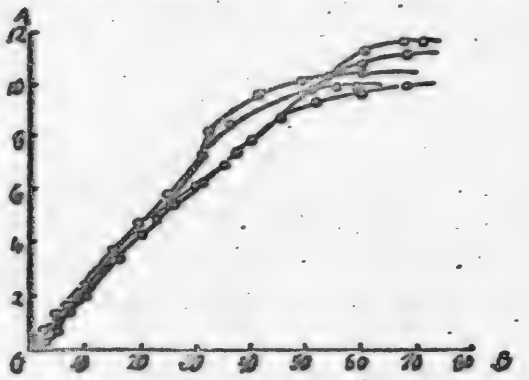

Fig. 13. Effect of adding 2% Na_2S upon the kinetics of the reduction of $Na_2SO_4 + SiO_2$ briquets in a current of carbon monoxide. Rate of gas flow = = 450 ml per min. Temperature 720°C.

A-Loss in wt., grams·10^{-1}; B-time, min.

The induction period for the reduction of $Na_2SO_4 + SiO_2$ is negligible in a current of hydrogen. The cited values for W_g indicate the variation of the reduction rate with the concentration of the H_2 and the CO.

Analysis of the quantity of Na_2S formed by the reduction of Na_2SO_4 in a current of CO usually indicates that the Na_2S represents 97-98% of the deoxidized Na_2SO_4. Hence, 2-3% of the Na_2S is hydrolyzed by moisture carried along in the CO. Analysis of the quantity of SiO_2 dissolved corresponds exactly to the quantity of Na_2S hydrolyzed. The hydrolysis of Na_2S in the hydrogen current constitutes tenths of a per cent of the deoxidized Na_2SO_4. Only in a strong current of hydrogen can the hydrolysis of the Na_2S be practically stopped.

Figure 13 indicates the effect of adding 2% Na_2S upon the induction period for the reduction of $Na_2SO_4 + SiO_2$.

We therefore see the complete similarity in the reduction of Na_2SO_4 by coal, CO, and hydrogen. It is apparent why coal that has been deprived of its volatiles begins to reduce Na_2SO_4 only at $t \geq 850°$, as Dudnikov has shown. In effect, pure carbon first burns to CO, which does reduce Na_2SO_4. Traces of H_2 or CH_4 in the products of combustion shorten the induction period, and the reduction of the Na_2SO_4 sets in at 700°.

In $Na_2SO_4 + SiO_2$ mixtures, the Na_2S that is formed is hydrolyzed by steam at the instant of reduction in accordance with the following equations:

$$Na_2S + H_2O = Na_2O + H_2S, \quad (8)$$

$$Na_2S + 2H_2O = 2NaOH + H_2S \quad (9)$$

The Na_2O or NaOH that is formed reacts with the SiO_2 without the steam participating in the reaction. Na_2SO_4 yields no sodium oxide during the process of its

reduction.

SUMMARY

1. A study has been made of the kinetics of the reduction of Na_2SO_4 with additions of 0.5, 1, 2, and 3 mols of C at temperatures of 750, 800, 900 and 1000°C. The rate of reduction rises as the temperature is raised, being but slightly affected by the percentage of carbon in the mixture.

2. It has been found that the temperature at which the reduction of Na_2SO_4 by coal sets in is 700°, provided the coal contains volatile matter or 0.1% producer gas tar is added to it. Adding up to 2% of Na_2S to the Na_2SO_4 + SiO_2 mixture likewise lowers the temperature at which reduction begins to 700°.

3. A similarity is noted in the kinetics of reduction with solid carbon and with gaseous deoxidizers. The participation of H_2 and CO in the reduction of Na_2SO_4 results in 1 mol of C being sufficient for the complete reduction of Na_2SO_4 in silica mixtures.

4. A mechanism is suggested for the reactions taking place in the Na_2SO_4 + SiO_2 + C system with water as an indispensable participant, to replace the obviously incorrect scheme proposed by Tamman and Olsen.

LITERATURE CITED

[1] P.P.Budnikov, Doklady Akad. Nauk. USSR, 1, 332 (1934).

[2] M.I.Nekrich, J. Appl. Chem. 11, 15 (1938).

[3] V.P.Ilyinsky, G.Ya. Tarasov, and A.A.Ginsburg, Trans. State Inst. Appl. Chem., 8, 80 (1932).

[4] Tammann u. W. Olsen, Z. anorg. u. allgem.Chem., 193, 245 (1930).

[5] G.Courtois, Compt. rend., 28, 277 (1939).

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THE SEPARATION OF SULFUR AND SELENIUM

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A large amount of sulfur is produced industrially by subliming pyrites from the flotation tailings of copper pyrites (in the parallel production of copper and sulfur) [1]. This sulfur, in contrast to the natural product, contains a considerable percentage of selenium (as much as 0.1%) and cannot be employed in the cellulose or paper industry [2]. This is why the separation of sulfur from selenium is of great practical importance. Moreover, extraction of the selenium is of interest in its own right because of the growing demand for this element.

Sulfur and selenium are analogs, and their separation is a difficult task. Up to the present time no simple and cheap industrial method has been proposed for the separation of these elements.

The sulfur-selenium structural diagram [3] indicates that in the molten state homogeneous solutions are formed; from which a large number of solid solutions settle out upon crystallization; that is why a mixture consisting of sulfur and selenium cannot be separated into its constituents by crystallization from the molten state.

Stepanov, Remnev, and Berger [4] have investigated a method of purifying the sulfur by oxidizing the selenium contained in it with nitric acid. In this method, the nitric acid is added, with stirring, to an emulsion of molten sulfur dissolved in magnesium chloride at 125°C. A disadvantage of this method is that the sulfur is oxidized at the same time as the selenium, resulting in a large, unprofitable consumption of nitric acid and in considerable losses of sulfur; this makes the method expensive and explains why it has not been employed in industry. We also find statements that efforts to use other oxidants have met with failure.

The experiments we made to separate sulfur from selenium in the molten and the gaseous states by means of selective adsorption on activated charcoal, silica gel, and other adsorbents, were not crowned with success.

The present paper reports on an investigation of the equilibrium in the melt-vapor system of mixtures of sulfur and selenium, with the objective of determining the feasibility of separating them by distillation.

EXPERIMENTAL

Chemically pure sulfur and selenium were mixed together in specified proportions and charged into the experimental apparatus (Fig. 1). The apparatus was made of Pyrex glass, with a nichrome winding around the outside for heating. The mixture was heated to boiling, the vapor being condensed in the upper part of the apparatus and draining off through a tube into a beaker. The condensate was analyzed to determine its selenium content. The amount of condensate taken was small, to keep the composition of the liquid phase as little changed as possible. The temperature was measured by means of a platinum - platinum-rhodium thermocouple, one end of which was immersed in the mixture. The boiling point was determined by the arrest point on the temperature curve during heating.

Tests were made with mixtures of various composition, ranging from 0.02 to 80% of selenium.

The test results are shown in Fig. 2, where the composition of the liquid phase is plotted along the axis of abscissas, and that of vapor along the axis of ordinates, both in per cent by weight. The graph shows that the melt contains a higher percentage of selenium than does the vapor above it, so that pure sulfur can be obtained in the distillate by repeated distillation or rectification, with selenium remaining in the residue.

Figure 3 gives the boiling point as a function of the composition of the mixture. The shape of the curve also indicates that no azeotropic mixtures exist and confirms the feasibility of separating these two constituents by rectification.

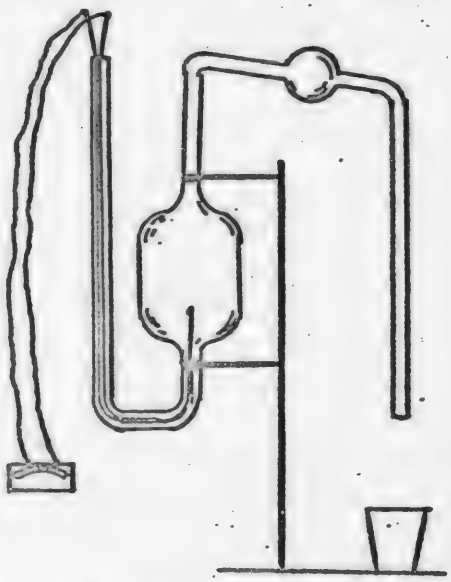

Fig. 1. Apparatus for distilling sulfur selenium mixtures at atmospheric pressure.

Evaluation of Results

In the molten state, sulfur and selenium mix in all proportions, and, according to Konovalov [5], the melt may be considered to be a binary solution of liquids that intermix without restriction and which do not interact chemically. In its general form, the mathematical expression for the partial pressures of the constituents in the vapor is as follows:

$$\frac{d \ln \gamma_1}{d \ln \gamma_2} = -\frac{1 - x}{x},$$

where γ_1 and γ_2 are the activity coefficients of the first and second constituents, respectively, and x is the mol fraction of the first constituent in the solution.

A special case of this equation, in which

$$\gamma_1 = \frac{p_1}{p_x} = 1,$$

results in the equation: $p = P_x x$

where p is the partial pressure of the constituent above the solution, and P is the

pressure of the saturated vapor of this constituent. So-called ideal solutions obey this law.

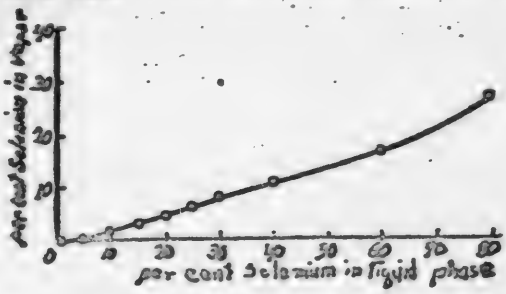

Fig. 2. Composition of the vapor as a function of the composition of the melt.

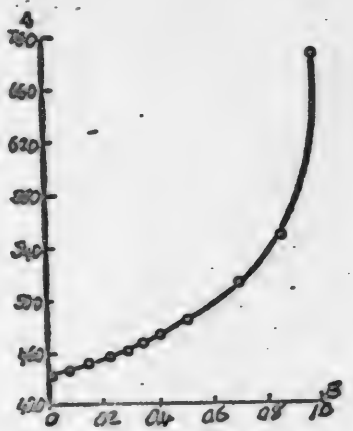

Fig. 3. Boiling point of a sulfur-selenium melt.

A-Boiling point of the mixture, °C; B- mol fraction of selenium in the liquid phase.

In our case, however, the system proves to be quite complex. Its complexity consists of the following: the vapor above the melt does not consist of the same molecules that are present in the liquid phase; as the result of dissociation, it contains molecules of different kinds, that are in equilibrium in it.

The data in the literature indicate [6] that close to the boiling point liquid sulfur consists of S_8 molecules, while selenium consists of Se_2 molecules. The molecular composition of the vapor is governed by the conditions for equilibrium among the molecules of differnet kinds for sulfur and for selenium at the given temperature.

These equilibria have been investigated by Preuner and Schupp [7], and by Preuner and Brockmoller [8], who found that the following equilibria are established in the temperature range 500-900°C:

$$3S_8 \rightleftarrows 4S_6, \quad S_8 \rightleftarrows 3S_2 \text{ and } Se_8 \rightleftarrows 3Se_2.$$

These authors give the following equations for the equilibrium constants of these reactions, K_1, K_2, and K_3:

$$\log K_1 = -\frac{89000 + 2T}{4.57 \cdot T} + 1.75 \log T + 4.3, \quad \log K_2 = -\frac{64000 + 4T}{4.57 \cdot T} + 3.5 \log T + 6.2,$$

$$\log K_3 = -\frac{56000 + 4T}{4.57 \cdot T} + 3.5 \log T + 2.4.$$

Hence, the following molecules will be present in the gas phase at these temperatures: S_8, S_6, S_2, Se_8, and Se_2.

Knowing the boiling point and the percentage composition of the vapor, as well as the equilibrium constants for the molecules of different kinds, from our experiments, we computed the partial pressures of all the different molecules above the melt at the latter's boiling point and the aggregate pressure, which equaled the barometric pressure. The results are shown in Figs. 4 and 5, in which for the sake of comparison we have also plotted the partial pressures for the S_8 and Se_2 molecules,

calculated from the law for ideal solutions. The graphs indicate that the actual partial pressures of the molecules in the vapor are higher, both for sulfur and for selenium, than the values calculated on the assumption that the system is an ideal one.

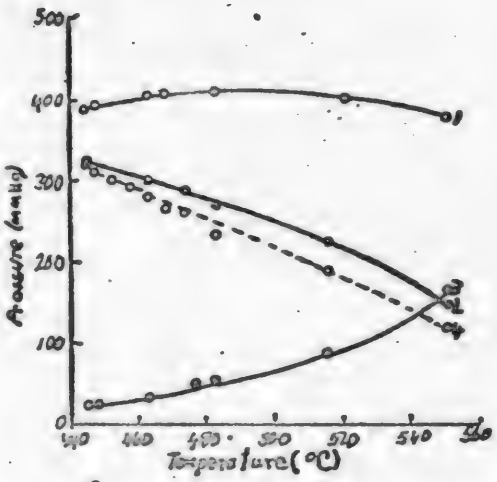

Fig. 4. Partial pressure of sulfur molecules above a sulfur-selenium melt at the boiling point.

1- p_{S_8}; 2- p_{S_8}; 3- p_{S_2}; 4- partial pressure p_{S_8}, computed from the law for ideal solutions.

Fig. 5. Partial pressure of selenium molecules above a sulfur-selenium melt at the boiling point.

1- p_{Se_2}; 2- p_{Se_2}, calculated from the law for ideal solutions (dashed line).

Activity Coefficients

Composition of the liquid phase, mol fractions		Activity coefficients	
Sulfur	Selenium	Sulfur	Selenium
0.984	0.016	1.004	7.0
0.968	0.032	1.009	4.52
0.921	0.079	1.03	2.1
0.847	0.153	1.06	1.5
0.777	0.223	1.08	1.35
0.712	0.282	1.11	1.2
0.649	0.351	1.12	1.1
0.59	0.41	1.15	1.05
0.48	0.52	1.2	1.02
0.29	0.71	1.25	1.01
0.133	0.867	1.27	1.005

The ratios of the partial pressures p_{S_8} and p_{Se_2}, obtained experimentally, to the partial pressures of these constituents calculated from the law for ideal solutions are nothing but the activity coefficients, which serve as a measure of the departure of a given system from the ideal. The activity coefficients for S_8 and Se_2 calculated in this manner proved to be greater than unity, which indicates that the given system's deviation from the ideal law is on the positive side (Table).

The experimental and calculated data showed that a melt of sulfur and selenium does not form an azeotropic mixture at any component concentration and can be completely separated by means of rectification.

Preliminary tests on the rectification of sulfur containing a small quantity of

selenium (0.05%) in a laboratory column made of hard glass demonstrated the feasibility of separating sulfur from selenium in practice by the method described.

SUMMARY

The conditions for equilibrium between the liquid phase and the vapor in the sulfur-selenium system have been investigated.

The activity coefficients for sulfur and for selenium have been found to exceed unity throughout a wide range of concentrations, which indicates the positive nature of the departure of this system from the law for ideal solutions.

No azeotropic mixtures are formed in the sulfur-selenium system, and it can be completely separated into its constituents by rectification.

LITERATURE CITED

[1] K.M.Malin. The Technology of Sulfuric Acid and Sulfur. United Scientific and Technical Press (1941).

[2] N.I.Nikitin and N.Ya.Solechnik. The Chemical Technology of Wood, Leningrad State Scientific and Technical Press (1941).

[3] Ringer, Z. allgm. u. anorg. Chem., 32, 183 (1902).

[4] M.N.Stepanov, S.N.Remnev, and N.N.Berger, J.Chem. Ind. USSR, 20, 4 (1941).

[5] D.P.Konovalov. The Vapor Pressure of Solutions. USSR Acad. Sci. Press, (1928).

[6] I.W.Mellor, A comprehensive treatise inorg. theor. Chem., 10, 23 (1930).

[7] G. Preuner, W. Schupp, Z. phys. Chem., 68, 129 (1909).

[8] G. Preuner, I. Brockmoller, Z. phys. Chem., 81, 129 (1913).

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PRODUCTS OF THE REACTION OF SILICATE GLASSES WITH HYDROFLUORIC ACID

N. G. Ozeretskovskaya

When hydrofluoric acid acts upon glass, a layer of difficultly soluble etching products is formed at the glass surface, screening the underlying glass from further action of the acid.. The latter acts upon that part of the surface of the glass that is not protected by these products. As a result, the surface of glass frosted by the acid is covered with innumerable hollows and elevations, which scatter light diffusely and produce the effect of a matte finish.

Obviously, a matte finish and, what is more, the deliberate control of the degree or nature of the matte finish may be achieved only if allowance is made for the growth, solubility, and form of the protective crystals and, above all, of course, their composition. The literature contains no precise information or unanimous opinion concerning their composition, in spite of the part played by the etching products in the etching of glass. Several authors [1,2,3,4] believe that the products of glass etching are fluosilicates of the metals. Other researchers [5] assume the simultaneous formation of fluorides and fluosilicates. Then there are assertions, not very well founded, to be sure, that some double fluorides are formed, such as a sodium-potassium fluoride [6]. The paper by Konigmann [7] shed a certain amount of light upon the problem of the chemical nature of the products of the reaction of glass with an etching solution, but even this paper confined itself to qualitative proofs, despite the convincing nature of the results adduced, the author not obtaining any quantitative characteristics of the crystals of etching products.

This circumstance led us, in turn, to examine the nature of these products. The data on the composition of the glasses we investigated are listed in the subjoined table.

Experimental procedure. The products formed in the reaction of glass with hydrofluoric acid are finely crystalline and possess quite definite crystallographic and crystallo-optical characteristics. We chose the refractive index of the crystals as the qualitative characteristic of the products of glass etching, since the determination of other crystallo-optical constants (such as the angle between the optical axes) is very difficult in crystals of small size.

To determine the refractive index of the crystals we made use of the immersion method, observing the shift in the Becke lines [8] in liquids with different refractive indexes. The refractive index was measured with an accuracy of $\pm$ 0.0001, the liquids used having a refractive index ranging from 1.3 to 1.7. One of these liquids was an individual substance, while the other was a mixture of two or more substances.

Before being used, the refractive indexes of the liquids used were always checked in an Abbe refractometer, which enabled us to measure them with a precision extending to the third decimal place. We used a parallel bundle of white light rays in our determination of the refractive indexes.

Glass No.	Composition of the glass, per cent by weight										
	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	CaO	ZnO	BaO	PbO	MgO	As_2O_3
1	65.88	–	–	10.22	–	23.65	–	–	–	–	
2	70.57	–	–	11.21	–	–	–	–	–	18.21	
3	46.70	–	–	7.42	–	–	–	45.88	–	–	
4	38.65	–	–	6.14	–	–	–	–	55.25	–	
5	59.52	–	–	9.45	–	–	31.03	–	–	–	
6	68.92	11.47	–	10.37	6.52	–	–	2.86	–	–	0.30
7	65.99	1.00	1.49	8.22	14.51	5.40	3.76	–	–	–	0.22
8	73.3	–	–	15.5	–	11.2	–	–	–	–	–
9	50.10	4.30	–	–	5.62	–	9.48	29.83	–	–	0.12
											0.55 Sb_2O_3
10	59.91	4.35	–	3.16	9.75	–	3.48	19.37	–	–	0.2
											0.57 Sb_2O_3
11	35.38	7.69	2.70	–	1.62	–	7.49	44.10	–	–	1.02
12	32.14	–	–	–	3.23	–	–	–	64.43	–	0.20
13	70	15	–	–	15	–	–	–	–	–	–
14	49.51	5.29	–	7.05	1.25	–	12.47	21.48	2.37	–	0.50
15	32.65	14.21	3.12	–	–	–	2.90	45.55	–	–	1.57
16	56.98	–	–	–	13.25	–	3.50	18.26	7.81	–	0.20
17	33.59	7.26	3.18	–	–	–	6.81	35.68	12.88	–	0.50
18	37.07	–	–	1.92	4.79	–	4.79	12.67	38.51	–	0.25
19	47.55	–	–	–	6.43	–	–	–	45.97	–	0.25

The preparation was gotten ready as follows. A small drop of a five per cent solution of hydrofluoric acid was placed on the polished surface of a glass sample of known composition. When the acid concentration was higher, the number of crystals formed was extremely great, but they were extremely small, and under these conditions it proved to be impossible to differentiate one crystal from another. After the reaction between the hydrofluoric acid and the glass was complete, a spot containing all the residual reaction products occupying the place of the drop of acid, these products were examined by polarized light under a microscope at a magnification of X320.

Products of etching soda glasses. Examination of the products of the reaction between hydrofluoric acid and a binary glass, whose composition was that of sodium bisilicate, showed that they consisted of hexagonal prisms with marked birefringence. Crystals of only one kind were produced, no others being found in the reaction of HF with sodium bisilicate. The refractive index of these crystals was lower than the refractive index of methanol (1.336). Since we did not have at our disposal liquids with a refractive index $n < 1.336$, we were unable to determine the refractive index of these crystals accurately.

Only crystals of this type were found in the products of the reaction of all the tested soda glasses (Nos. 1-8, 10, 14, and 18) with hydrofluoric acid. Sodium fluosilicate crystallized in exactly these crystals, as was demonstrated by examination of a preparation of this salt that had been repeatedly recrystallized from

water in order to increase the dimensions of its crystals. Under no circumstances could these crystals have been confused with those of any other sodium salt.

Thus when glass is reacted with (5%) hydrofluoric acid, its soda component forms a fluosilicate.

Products of etching potash glasses. When all the glasses containing potassium (Nos. 6, 7, 9-14, 16, 18 and 19) were reacted with hydrofluoric acid, the crystals formed all were of the cubic system typical of potassium compounds, exhibiting absolutely no detectable birefringence. The refractive indexes of the crystals ranged from 1.338 to 1.341. Potassium fluosilicate, which we studied under the microscope in two samples: one the recrystallized commercial product, and the other a precipitate secured by reacting zinc fluosilicate with potassium chloride, crystallizes in crystals of exactly that shape with the same refractive index.

Thus, when glass is reacted with hydrofluoric acid, its potassium constituent forms a fluosilicate as the sodium component does. It should be pointed out that this conclusion was recently confirmed by the research of Totesh. Totesh checked the foregoing results of our researches on glasses of the following binary systems: $Na_2O \cdot SiO_2$ and $K_2O \cdot SiO_2$, and got the same characteristics for the crystals of the sodium and potassium compounds as we had. She also confirmed the fact that the alkaline constituents of glass formed fluosilicates by X-ray analysis of the products in question.

Products of etching barium glasses. When the glass containing barium (No. 11 in the table) was reacted with hydrofluoric acid, it yielded minute elongated crystals that exhibited double refraction and direct extinction. Their refractive index along the short axis was 1.435; it was somewhat higher along the long axis. Because of their specific form, these crystals can be distinguished in the products of glass attacked by hydrofluoric acid even when the percentage of barium is slight (some 3% by weight). When glass that is rich in barium is etched, these crystals cover the entire surface of the etched spot. A check with a preparation of barium fluosilicate showed that the latter forms crystals of exactly the same type, the same form, and the same refractive index (unknown in the literature) as those observed by us.

Hence, when reacted with HF, the barium constituent in a glass forms a fluosilicate.

Products of etching glass containing calcium. The products of the reaction of glasses containing calcium (Nos. 1, 7, 8) with hydrofluoric acid contain acicular, elongated crystals that seem to have been sheared off at the ends, with slight birefringence, which are partially soluble in alcohol. Their refractive index is 1.387 (along the longitudinal axis). As a study of a preparation of calcium fluosilicate, these crystals are identical in form and refractive index (unknown in the literature) with the crystals of this preparation. Hence, the calcium constituent of glass forms a fluosilicate when the glass is treated with hydrofluoric acid.

Products of the etching of lead glass. An effort to investigate the products of the reaction of lead glass with hydrofluoric acid by the immersion method met with failure. This is due, first, to the extremely small dimensions of the crystals formed by the etching products typical of lead; and second, by the unusual abundance of these crystals, besides the apparently readily formed aggregates. These crystals' forms are indeterminate, but they are so numerous as to interfere even with the determination of the refractive index of the crystals of other compounds formed alongside them when hydrofluoric acid acts upon flint glass. We were wholly unable to measure their own refractive index. The dimensions of the crystals were not increased noticeably even by extremely slow recrystallization (this was done during

48 hours at low temperature, in a Dewar flask, at a rate of about 3° per hour).

Some data on the chemical analysis of the etching products. In addition to the use of the immersion method, the nature of the compounds formed when glass is reacted with hydrofluoric acid was determined by using qualitative analysis. The insoluble products of the etching of four glasses: lead (No. 19), borosilicate (No. 6), calcium (No. 7), and barium (No. 14) by a 40% solution of hydrofluoric acid were analyzed. These precipitates were filtered out, repeatedly washed with water, and dried before analysis. Part of the precipitate was fused in a platinum crucible with soda (1 part of precipitate to 6 parts of soda) in order to recover the silicic acid. After it had solidified, the melt was leached out with water acidulated with hydrochloric acid, and the precipitated silicic acid was filtered out. The SiF_6 ion was detected in a separate sample.

The analysis showed: the lead ion in the products of the etching of glass No. 19; the calcium ion and traces of the barium ion in the products of glass No. 6; the potassium and calcium ions in the etching products of glass No. 7; and ions of lead, barium, and potassium in the products of glass No. 14. SiF_6'' was found in the etching products of all the glasses, with the exception of glass No. 19. Comparison of the results obtained by both methods - the immersion method and qualitative analysis - yielded the following information.

The finding of potassium and SiF_6 ions in the etching products of glasses No. 6 and 7 that were insoluble in HF corroborates the conclusion, reached on the basis of the results of the immersion method, that potassium fluosilicate is formed in these reactions. Similarly, the presence of ions of potassium, barium, and SiF_6 in the insoluble etching products of glass No. 14 indicates the formation of the respective fluosilicates (potassium and barium).

Thus, the data of both methods are in complete agreement with regard to the nature of the products yielded by the reaction of potassium and barium constituents of glass with hydrofluoric acid. The results of analysis of the insoluble products of Glass No. 19, namely: the finding of lead ions in large amounts, may indicate solely that lead fluoride is formed when this glass is reacted with hydrofluoric acid. Lead fluosilicate is a readily soluble salt [10], and hence it cannot constitute the bulk of the precipitate of the insoluble products of lead glass, which had been repeatedly washed with water. The data in Honigmann's paper [7] on the solubility of fluorides and fluosilicates in hydrofluoric acid corroborate this conclusion, pointing out as he does that lead fluoride is immediately precipitated when $PbSiF_6$ is dissolved in HF. The presence of PbF_2 in the products of the etching of lead glass is also confirmed by the results of Totesh's X-ray analysis of glasses in the binary system $PbO \cdot SiO_2$.

A discrepancy exists between the results we obtained by the immersion method and by the qualitative analysis of the etching products in the case of the calcium constituent of glass. According to the immersion method, calcium fluosilicate is formed, whereas the results of the qualitative analysis indicate the formation of calcium fluoride, inasmuch as the calcium ion was found in the products of the etching of glass No. 7 that were insoluble in HF. We also know that calcium fluosilicate is a salt that is readily soluble in water, but is rapidly converted into the insoluble fluoride in a solution of hydrofluoric acid [7].

A similar assertion is made by Herbert [5]. According to Herbert, the $CaSiF_6 + 2HF \rightleftarrows CaF_2 + H_2SiF_6$ reaction is reversible, the concentration of calcium in the solution depending upon the concentrations of the two acids. The author states that when HF acts upon a soda-potash glass, the solution remains transparent for only a few minutes, after which it grows turbid owing to the formation of calcium fluoride,

Sauka [9] has recently succeeded in growing crystals of PbF_2, but his method cannot be employed in our case.

the latter being precipitated almost quantitatively. But as the concentration of HF falls and that of the H_2SiF_6 correspondingly rises, the calcium fluoride begins to redissolve, and minute crystals of $CaSiF_6$, etc., can be recovered from the solution.

Hence, Herbert's data lead us to expect both the fluosilicate and the fluoride of calcium as the products formed when HF acts upon the calcium component of glass.

In this light, there is every reason to consider the discrepancy noted above in the data of the two methods as merely an apparent one. It is due, obviously, to the fact that the etching products subjected to qualitative analysis were secured after they had been in contact with a concentrated solution of HF for a long time, whereas the products tested by immersion method had been formed as the result of the nearly instantaneous reaction with drops of hydrofluoric acid that had been dilute from the very start.

SUMMARY

1. It has been established that when hydrofluoric acid acts upon glass, the latter's sodium, potassium and barium constituents form the corresponding fluosilicates.

2. In this reaction the lead constituent in the glass forms lead fluoride.

3. When calcium glasses are reacted with HF, calcium fluosilicate or calcium fluoride may be formed, depending upon the prevailing conditions (acid concentration).

4. The optical characteristics of barium and calcium fluosilicate crystals, previously unknown in the literature, have been obtained.

In conclusion, I wish to express my deep gratitude to Academician I.V.Grebenshchikov for his guidance of this research and his valuable advice during its preparation for publication.

LITERATURE CITED

[1] Reinitzer. Abstract, J.Soc.Chem. Ind., 5, 669 (1886).

[2] Tillotson, J. Ind. Eng. Chem, 9, 937 (1917).

[3] Doerinkel, Glastech. Ber., 9, 268 (1930).

[4] Fenske u. Koref, Wiss. Abhandl. Ceram Konz., 2, 270 (1931).

[5] Herbert, Compt.rend., 199, 369 (1934).

[6] Hesse. Die Glasveredelung (1928).

[7] Honigmann, Glastech. Ber. 10, 154 (1932).

[8] Rinne and Berek. Optical Investigations with the Polarized Microscope. United Scientific and Technical Press (1937).

[9] Sauka, J. Gen. Chem. 19, 1453 (1949).*

[10] Kausch. Flussaure, Kieselflussaure und deren Metallsalze (1936).

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* See CB translation p. 1453 ff.

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CLASSIFICATION OF REACTIONS BETWEEN SOLID SUBSTANCES

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Many reactions of importance in engineering involve, as we know, solid substances.

Many of these reactions involve so-called "solid-phase" * processes, i.e., reactions that take place in a mixture of solid substances.

These reactions, which include many processes in metallurgy, the technology of the silicates, and the manufacture of various other inorganic substances, have been the subject, not without cause, of persistent investigation by numerous researchers during the past 25 years.

A number of problems involving various processes in the reactions of solid substances that are important from the theoretical and practical standpoints have been resolved as the result of these investigations. Light has been shed upon many extremely important and interesting phenomena, especially as the result of the work done by D.S.Belyankina, P.P.Budnikov, A.S.Berezhny, B.B.Yerofeev, N.A.Toropov, V. F.Zhuravlev, A.I.Avgustinik, V.A.Mazel, I.S.Lileev, and other Soviet research workers. Still, many problems remain unsolved even now, demanding study and solution. One of the most important of them all is the problem of the classification of solid-phase processes.

This problem, despite all its importance and complexity, has been touched upon in only a few papers, which have not resolved it adequately. The researches of W. Jander, W.Muller, G. Kuttig, W. Jost, and W. Garner on the systematization of the reactions that involve solid substance, which we know from the literature, unfortunately do not meet contemporary standards of knowledge of "solid-phase" processes, not covering them fully, starting in part from false assumptions and thus being unable to serve as a dependable tool in the further study and development of these processes. Moreover, if we rely upon some of these researches (which played a great positive role in their time) at the present time, they may act as a brake upon the study and technical evolution of the processes in question.

* The correctness of the use of this term is sometimes rather relative, for the reacting substances actually remain solid from the beginning to the end of the reaction in far from all the reactions usually classed as solid phase ones.

It therefore seemed to be very useful to make a critical survey of the basic researches on the classification of "solid-phase" reactions.

Among the papers touching on this problem in one way or another, we must first mention the paper published in 1938 by S.Z.Roginsky [1], which was of considerable importance at the time, in which the author formulated the principles governing the classification of topochemical reactions (discussed below).

The first attempt to systematize solid-phase reactions was undertaken more than 20 years ago by Jander [2]. The classification he proposed was founded on the nature of the chemical reaction between solid substances; Jander thus divides the reactions between solid substances into the following groups.

1. The reaction of a basic oxide with an acid one: for example, such oxides as BaO, CaO, SrO, MgO, ZnO, PbO, CdO, NiO, FeO, CoO, CuO, etc., with one of the acid oxides, such as WO_3, MoO_3, SiO_2, TiO_2, V_2O_5, Fe_2O_3, etc., as in:

$$BaO + WO_3 \longrightarrow BaWO_4.$$

2. The reaction of a salt of carbonic or sulfuric acid with a basic oxide, accompanied by a shift of the anhydride from the acid to the oxide: such as strontium, calcium, or magnesium carbonates with barium, strontium, or calcium oxides, and of the sulfate of Ca, Sr, Mg, Co, Ag, Pb, and Cu with the oxides of Ba, Sr, Ca, Pb, Mg, etc., as in

$$Ag_2SO_4 + PbO \longrightarrow PbSO_4 + Ag_2O.$$

3. Replacement of the CO_2 in a carbonate by a solid acid oxide: such as the reactions between $CaCO_3$, $SrCO_3$, $BaCO_3$ and SiO_2, MoO_3, and WO_3, as in:

$$CaCO_3 + MoO_3 \longrightarrow CaMoO_4 + CO_2.$$

4. Replacement of the metal in a salt, oxide, or sulfide by another metal, such as occurs, for example, when magnesium is heated with the oxides of zinc, tellurium, cadmium, or copper; aluminum with the oxides of zinc, cadmium, copper and nickel; Zn with CuO, PbO, or AgI; Fe with PbO or CuO; Pb with CuO, and so forth, as in $Mg + ZnO \rightarrow MgO + Zn$.

5. Double decomposition when a carbonate is reacted with a sulfate, as in:

$$BaSO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + BaCO_3.$$

This separation and grouping of reactions performed by Jander is of greater historical than theoretical or practical importance today.

In fact, it is not hard to see that the reactions of Group 2, in which part of component A splits off and is added to component B, is similar to the reactions in Group 4, in which the same phenomenon occurs. The difference between the chemical composition of the part split off from A and transferred to B is unessential for the systematic classification of chemical reactions, for its composition is not governed by the fundamental nature of the kinetic laws controlling the process.

Finally, many of the technically important reactions involving solid substances, such as the reactions involving the reduction of metal sulfates by carbon, the reactions of phosphates with metallic oxides, etc., are completely missing in Jander's classification.

It is obvious that such a classification system, which records some general features (dealing chiefly with the chemical composition of the initial components) of some solid-phase processes, cannot serve as the basis for a profound study and generalization of all such processes.

An attempt to classify chemical reactions according to a technological standpoint

was once made by Müller [3]. Bearing in mind that in general it is possible for a solid to react with a solid, a liquid, or a gas, a liquid with a liquid or a gas, and a gas with a gas, and a solid with a liquid and a gas at the same time, Müller divides all chemical reactions into 7 classes in accordance with the foregoing listing. Then, considering that the reaction of any two bodies (say, a solid with a solid) may yield 7 different products (depending upon the combinations of the states of aggregation), he differentiates 7 kinds of reactions within each class.

Thus, Class 1 in Müller's system (solid + solid) looks like this:

1) $S + S \rightarrow S + S$,
2) $S + S \rightarrow S + L$,
3) $S + S \rightarrow S + G$,
4) $S + S \rightarrow L + L$,
5) $S + S \rightarrow L + G$,
6) $S + S \rightarrow G + G$,
7) $S + S \rightarrow S + L + G$.

As a result, the number of kinds of reactions in all the classes totals 49.

Having purely practical objectives in mind, Müller allowed for certain simplified notions of chemical processes in his classifications. For instance, he does not distinguish between the concepts of a "solid" (one) and a "solid + solid" (two), and hence between the processes:

a) Solid $\rightarrow$ solid + gas, and

b) Solid + solid $\rightarrow$ solid + gas.

In this connection, owing to external features that do not correspond to the essence of the phenomena, he has the reaction of the dissociation of calcium carbonate come under the same heading as its reaction with kaolin, giving rise to silicates and other calcium compounds and evolving CO_2, which have very little in common with each other.

Furthermore, in his assignment of a reaction to one kind or another, Müller is guided solely by the initial and final states of aggregation of the system's components, and he does not even follow this rule exactly in every case.

For example, he assigns the reaction

$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$

to the reactions of the kind $S + S \rightarrow S + G$, whereas $NaHSO_4$ is a liquid at the temperature at which it reacts with NaCl.

For the same reason the reaction

$$CuO + C \rightarrow Cu + Co$$

is evaluated in this classification as proceeding by the interaction of a solid with a solid, whereas it is much more likely in that instance that it takes place chiefly in the gas phase:

$$Co + CuO \longrightarrow Cu + CO_2,$$
$$Co + C \rightleftarrows 2CO,$$
$$\overline{CuO + C \longrightarrow Cu + Co.}$$

This is how modern metallurgy [4,5] deals with the processes involving the reduction of metallic oxides by solid carbon.

Nor can the possibility of dissociation of the copper oxide, with the ensuing

binding of the oxygen by the carbon, be wholly excluded in this case.

Moreover, because of the circumstance mentioned above (the simplified characterization of processes according to purely external features), Müller wrongly classes the Leblanc process, according to its overall equation:

$$Na_2SO_4 + 4C + CaCO_3 \longrightarrow Na_2CO_3 + CaS + 4CO,$$

which does not reflect the actual course of the interaction between the reagents and the intermediate processes, as a reaction of the type:

$$\text{Solid} + \text{solid} \rightarrow \text{solid} + \text{liquid} + \text{gas},$$

and so forth.

It is a matter of course that such a simplified classification, which might satisfy the needs of some narrow practical requirements and problems, cannot aid in the generalized scientific investigation of solid-phase processes.

Jost [8] divides reactions between solids into the following classes.

A. Interaction between two elements (in practice, according to Jost, this can apply only to metals), giving rise to compounds of the type

$$M' + M'' \longrightarrow M'M'' \text{ or } mM' + nM'' \rightarrow M_m' M_n''.$$

B. Interaction between two compounds having the same common (like) component (an element, an ion, or a complex), such as:

$$mM'X' + nM'X'' \longrightarrow (M'X')_m(M'X'')_n$$

or

$$mM'X' + nM''X' \longrightarrow (M'X')_m(M''X')_n.$$

C. Interaction between two compounds that have no component in common, as:

$$M'X' + M''X'' \longrightarrow M'X'' + M''X'.$$

Jost then subdivides each class into groups (subclasses), depending upon the possibility that solid solutions are formed in the system, as well as on their nature, such as:

1) The original substances and their products (i.e., all the components in the system) form solid solutions with unrestricted solubility, i.e., they mix with one another without restriction:

2) The original substancesand their products form solid solutions with restricted solubility;

3) Part of the components of the system, say, the original substances, do not form solid solutions; and

4) Neither the original substances nor the end products form solid solutions.

The kinds of reactions are then further distinguished in this classification according to the differences in the mobility (rate of diffusion) of the elements (complexes) of the M', M'', and the X', X'' type.

Thus, Class B, Group (Subclass) 4 comprises the following kinds:

a) M' and M'' are more mobile than X' and X'';

b) M' and M'' are less mobile than X' and X''

Jost rightly considers that the structural diagram of a system must be borne in mind when assigning the latter to one class or another.

But when we examine Jost's classification tables [6], we notice the following:

1) Much of his systematic classification is devoted to purely diffusional processes for the formation of solid solutions, which are not related to chemical reactions properly speaking;

2) Confining himself to processes that take place solely in the solid phase, his classification system actually does not classify solid-phase chemical reactions;

3) The differences in the mobility of M', M'' and X', X'' do not essentially affect the nature of the processes or the phenomena that go to make it up.

It should be noted that the field of application of this classification is limited to a few, chiefly metallurgical, processes. Any attempt to generalize or to subdivide many other solid-phase processes in more or less detail on the basis of this classification is doomed to failure.

S.Z.Roginsky made a study of topochemical reactions and suggested that they be classified as follows:

I. Reactions involving the decomposition of a crystalline body into gaseous products.

II. Reactions involving the formation of crystals from a homogeneous (gas or liquid) phase.

III. Topochemical reactions in the narrow sense of the term, characterized by the presence of solids both in the original constituents and in the reaction products.

In this scheme, the reactions of Class I are really " solid-phase" while the Class I and Class II reactions may be entered as component parts of the Class III reactions. As S.Z.Roginsky points out, the Class III reactions differ widely in their chemical nature, including a wide range of processes, from allotropic transformations and the breakdown or formation of compounds such as the crystal hydrates and the ammoniates (for which no chemical heat of activation need be expected) to reactions such as the reduction of oxides and sulfides and the decomposition of salts with complex anions, i.e., to reactions involving profound chemical transformations (for which an appreciable true heat of activation may be expected).

What is characteristic of reactions of this class is the existence of at least two solid phases.

The important classification principle noted by S.Z.Roginsky, who did not attempt, by the way, to make a comprehensive classification of solid-phase processes, was often utilized by other investigators subsequently.

Garner [7,8] somewhat extended and slightly supplemented the classification suggested by S.Z.Roginsky, classifying the reactions involving solid substances as follows:

1) Reactions that are not related to the reconstruction of the crystal lattice, i.e., taking place without a change in the solid phase, including: a) reactions in which the resulting product forms a solid solution with the initial reagent; and b) reactions of chemosorption at the surface of the solid;

2) Reactions that include one stage of crystallization; they comprise the interaction of gases resulting in the formation of solid substances, as well as the formation of the latter when solutes are combined;

3) Reactions in which the crystal lattice is disrupted, as in the decomposition of mercuric oxide, potassium azide, etc., in which the solid phase disappears

completely, yielding gaseous products; and

4) Reactions involving both the disruption and the formation of a crystal lattice; as Garner states, these reactions, which constitute an extremely extensive class, include the following types:

a) $A_S \rightarrow B_S + Gas$,

for example, the decomposition of a photographic emulsion under the action of light;

b) $A_S \rightarrow B_S + C_S$,

say, the decomposition of silver acetilide; and

c) $A_S + B_S \rightarrow C_S$,

say, the formation of spinel from a mixture of oxides.

This listing merely outlines the principles of the classification, leaving out a large number of important transformations in the field in question, such as, $A_S + B_G \rightarrow AB_G$, $A_S + B_L \rightarrow AB_S$, and others. It is apparent that Type 4c covers a wide range of solid substances. As yet, a detailed classification of these very reactions would be of great interest.

According to Hüttig [9], who suggested a general classification of chemical reactions not so long ago (1941), assigning a large area of the classification to the transformations that involve solid substances, these reactions fall into five classes, each of which is further divided into a substantial number of subclasses, which in turn include an extraordinarily large number of types and varieties (subtypes) of reactions.

There are more than 100 types (which are further subdivided into subtypes) of reactions in some of the subclasses in Hüttig's classification. This circumstance makes difficult even the slightest detailed discussion of his classification system and compels us to confine ourselves to a brief characterization of some of its features.

Hüttig chose the number of "component parts" in the reaction system as the basic criterion for assigning a process to one class or another.

For instance, the production of soda, represented by the following overall reaction:

$$Na_2SO_4 + 4C + CaCO_3 \longrightarrow Na_2CO_3 + CaS + 4CO,$$

falls under Class V, according to Hüttig, because he considers this process to contain 5 component parts:

I = Na, II = S, III = O, IV = C and V = Ca.

Hüttig assigns this process to the type represented by the following equation:

$$ABC_S + D_S + EDC_S \longrightarrow ADC_S + EB_S + DC_G.$$

In fact, since the foregoing equation represents merely the sum total of a number of reactions actually taking place in this process, however, the latter cannot be assigned to any one class on the basis of that equation. Other reactions take place in this process, which have to be classified.

The same objection holds for the assignment of most other processes to Classes III, IV, and V.

As for the types of reaction (involving solid substances), Hüttig's classification, which lists several hundreds of them, divides them according to the state of

aggregation of the initial constituents and the reaction end products.

Lastly, the subtypes are classified according to the differences in the state of aggregation of the intermediate products of the reaction.

It should be noted that the fundamental classification principle adopted by Hüttig compels him to assign to the same class processes that have nothing in common but the number of "component parts" in the overall equation for the process. This hampers Hüttig in the process of further classification as well. Thus, in his classification system Subclass B_{III} (substitution reactions) of Class III, numbering 89 different types of reactions, includes the following, for example:

1. $AB_S + C_S \rightarrow AC_S + B_S$
   (Example: $CuSO_4 + BaO \rightarrow BaSO_4 + CuO$).

3. $AB_S + C_S \rightarrow AC_S + B_L$
   (Example: $2SO_3 \cdot 3HgO \cdot 2H_2O + HgI_2 \rightarrow 2SO_3 \cdot 3HgO \cdot HgI_2 + 2H_2O$).

13. $AB_S + C_S \rightarrow AC_G + B_S$
   ($FeO + C \rightarrow CO + Fe$).

38. $AB_L + C_S \rightarrow AC_S + B_G$
   ($H_2SO_4 + 2K \rightarrow K_2SO_4 + H_2$, with no water present).

43. $AB_S + C_G \rightarrow AC_G + B_S$
   ($3Fe_2O_3 + H_2 \rightarrow H_2O_{steam} + 2Fe_3O_4$).

51. $AB_L + C_S \rightarrow AC_L + B_L$
   ($PbS_{fused} + Fe \rightarrow FeS + Pb$).

52. $AB_L + C_L \rightarrow AC_L + B_S$.

71. $AB_L + C_G \rightarrow AC_L + B_G$.
   ($CaI_{2fused} + Cl \rightarrow CaClI_2 + I$).

Thus, this subclass comprises reactions that take place in entirely different ways (such as reactions 1 and 52, 3 and 71, etc.) and, as we may readily imagine, obey different kinetic laws.

Moreover, quite similar reactions can be found in different classes of this classification, as in Classes II, III, and IV.

Because of this, Hüttig's paper is actually nothing but a formal listing of all conceivable varieties of reactions, despite its thoroughness, which of course limits its applicability.

The foregoing covers the principal papers on the systematic classification of the reactions that involve solid substances.

It is readily seen that the classifications differ considerably.

The main reasons for these differences are the different objectives the various authors were pursuing in their research.

Müller, for instance, had purely technological aims in view, believing that processes of the same kind ought to require about the same instrumental and technological setup.

It was Garner's objective, practically speaking, to do little more than expand Boginsky's fundamental ideas on the subject of solid-phase processes without going into a further systematization of these ideas.

Jander was interested in grouping solid-phase reactions according to the similarity of the chemical actions involved.

Jost felt it necessary to stress the presence and the nature of the solid solutions in solid-phase systems.

Lastly, Hüttig endeavored to provide an all-inclusive listing of all possible varieties of reactions, taking into account first the "component parts" of the reaction mixture, then the state of aggregation of the substances, and so forth.

The modern theory of heterogeneous chemical processes endeavors, as we know, to discriminate and generalize them according to criteria that are determined by the fundamental laws governing their course.

From this point of view, what is most important is a search for criteria of such physical and chemical similarities or differences between individual "solid-phase" processes that would enable us to describe their kinetics, more or less accurately, in terms of some common or differing equations, respectively.

It is obvious that all the classification systems discussed above do not satisfy this requirement and are very far from a solution of such a problem.

This made it apparent that a new classification system of "solid-phase" reactions had to be developed.

In working out such a classification system we had to start with the nature of the fundamental "elementary" phenomena, which underlie the processes to be classified, for the kinetics of the latter will, or course, be determined by the laws governing their constituent phenomena.

These may be: a chemical reaction, a rearrangement of the substance, or a change in the substance's state of aggregation.

It is evident that different combinations of these phenomena will result in d different overall processes in mixtures of solid substances. The number of such combinations may be fairly large. But this large number of combinations may include quasi-borderline cases, in which the process rate is limited by some one of the phenomena named. In these simple cases, the kinetics of the whole transformation may be described by the equation for the velocity of the respective physical or chemical process.

Thus, if the rate of transformation is limited by the evaporation (or sublimation) of some substance consisting of spherical particles, it is determined by the following equation:

$$\frac{dG}{d\tau} = K\,(1 - G)^{1/3},$$

where G is the degree of transformation of the substance, the evaporation of which limits the process rate; τ is the time; and K is a constant depending upon the properties of the reagent and the process conditions. If the limiting stage of the process is the diffusion of the reagents among spherical or nearly spherical particles (the diffusion region), this rate will be expressed by [10]:

$$\frac{dG}{d\tau} = K\,\frac{(1 - G)^{1/3}}{1 - (1-G)^{1/3}}.$$

This equation has been derived from the equation for the rate of evaporation of spherical drops of constant radius, which is well known in physics.

If physical phenomena have practically no effect upon the process rate, the latter is determined by the equation of the chemical kinetics during the course of the reaction (the kinetic region), as in a first order reaction, etc.

Hence, the kinetic laws governing all such simple processes in the transformation of mixtures of solid substances can be expressed by means of a few equations. It is thus evident that the kinetics of "complex" processes, dealing with the transitional, intermediate region, will be expressed by a combination of these equations that allows for the part played by all the phenomena that determine the process rate.

A comparatively large number of such combinations is theoretically conceivable. The overwhelming majority of actual "solid-phase" processes of any practical interest, however, may be regarded without substantial error as "simple" ones that obey the respective laws for the simple phenomenon limiting the course of one process or another.

This latter circumstance may serve as the foundation for developing a systematic classification of "solid-phase" processes, inasmuch as the latter's major purpose must be the generalization and classification of reactions possessing practical significance. The one thing that must be borne in mind is that in practice the velocity of a single process may be limited by different phenomena in its various stages and, hence, it may obey various laws.

It is obvious from the foregoing that the classification of "solid phase" reactions according to the proposed principle necessitates knowing the principles underlying their mechanisms.* In particular, we must bear in mind that many so-called solid-phase processes actually involve the participation of gaseous and liquid substances, which arise and then vanish during the course of the reaction. Hence, the development of a classification of "solid-phase" reactions must allow for the possibility that such phenomena as fusion, sublimation, dissociation, etc., occur during the process of the transformation of a solid mixture.

Thus, the objects of the classification are processes in which the original substances and some of the products are solids, while liquid and gas phases may occur during the course of these processes.

Amplifying the concept of the chemical phenomena (reactions) and physical phenomena (rearrangement of the substance's particles and a change in its state of aggregation) that constitute these processes, we may set down that they boil down to the following in practice:

1) A chemical reaction, 2) diffusion, 3) sublimation or evaporation, 4) fusion, and 5) crystallization.

Some of these phenomena (such as, say, the first) constitute an essential part of every interaction in a mixture of solid substances, while others (such as the second) play an essential role in most such reactions, and still others (3,4,5) may or may not be present. But in every case the kinetics of the entire transformation will be practically determined by the laws governing the course of its limiting stage.

Assuming that any of the listed phenomena may play this part, we may accordingly conceive of 5 classes of reactions, theoretically in a mixture of solid substances.

The subclasses are defined by the presence of different variants for the course of each phenomenon that are responsible for a fundamental difference in its kinetics.

The rate of fusion of solid substances and their crystallization from a melt, which depend upon several factors, are governed in practice by the rate at which the

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*The problem of the mechanism of the reaction between solid substances, which has been dealt with in several papers by the present authors, will be discussed in detail in other reports.

heat of fusion is imparted to the particles of these substances or at which heat (of crystallization) is taken away from them. It is obvious that limiting the supply or removal of heat may slow down these processes just as much as endothermic or exothermic reactions or other phenomena entailing an appreciable joulean effect.

Still, in comparison with the velocity of other phenomena, the rate of heat transfer between the particles of the reacting substances that are heated to the reaction temperature and the surrounding medium is usually much too high to play any material role in determining the kinetics of the process. Thus, fusion and crystallization from a melt mostly take place much more rapidly than the first three phenomena listed above.

The velocity of the chemical reaction proper, which is governed by the chemical properties and the percentages of the original substances in the reaction mixture, may vary within extremely wide limits, as we know. The rate of the diffusion, which depends upon the physical properties of the substances and the thickness of the diffusion layer, may likewise take on different values (usually very small ones). The rate of evaporation (or sublimation) of a substance may vary within a wide range, depending upon its vapor pressure and the dimensions of its particles.

The foregoing indicates that it is apparently enough for all practical purposes to subdivide all reactions taking place in a mixture of solid substances into three large classes:

I. Those limited by chemical reaction (more precisely, by the velocity of the chemical reaction).

II. Those limited by diffusion.

III. Those limited by evaporation or sublimation.

Class I of this list includes many processes in which the part played by physical processes is minor owing to the low rate of the chemical interaction proper, the negligible thickness of the diffusion layer, the high values of the diffusion coefficients, and similar causes.

Class I reactions may, in practice, include any of the following five phenomena, which define the five subclasses of processes, respectively, in this class:

1) A first-order reaction.

2) A second-order reaction.

3) Interaction at a constant concentration of the reacting substances, as well as a zero-order reaction.

4) An autocatalytic reaction.

5) Several successive reactions.

Subclass 1 of Class I includes, in particular, dissociation reactions, which are extremely important in many so-called solid-phase processes; among many other processes, Subclass 2 includes several polymorphic transformations that are very important in the technology of the silicates; and Subclass 3 includes interactions between two solid substances and reactions between a solid and a liquid when the latter's concentration remains constant (due, for example, to the composition of the system, which fuses at the process temperature), etc.

Class II comprises most of the so-called solid-phase processes involving the formation of a sufficiently substantial diffusion layer of the reaction product upon the particles of some reagent.

Class III includes some processes involving the formation of spinels, sulfides, and other compounds, limited by the evaporation or sublimation of some substances. More particularly, many processes involving the reaction of a basic oxide with an acid oxide, which Jander included in Group 1 of his classification, apparently belong here.

Thus, the principle described may be employed to classify all "solid-phase" reactions that are of any practical importance. The only thing that must be borne in mind is that, as has been said above, a single chemical transformation of a mixture of solid substances may come under the heading of one or another of these classes in various stages of the process, depending upon the relative values of the various resistances (chemical, diffusional, etc.) present in the process.

It is obvious, for example, that some processes that involve the formation of a diffusion layer of the product, which fall under Class I or III during their initial stage, become Class II processes when the diffusion resistance reaches a certain value. And during a certain period, depending upon the nature of the process and the conditions under which it is taking place, it may occupy a position intermediate between Classes I and II or III and II.

SUMMARY

1. The well-known systems for classifying the reactions between solid substances elaborated by Jander, Garner, Hüttig, and other researchers, cover only part of these processes, as a critical analysis of these classification systems indicates, and represent largely nothing but a formal listing of the processes.

2. All these classification systems, which differ substantially from one another, are constructed upon assumptions that do not accord with the modern theory of heterogeneous chemical processes and have one feature in common: they do not classify "solid-phase" processes by their most important features, which can specify the basic laws governing the course of these processes, but by secondary, and sometimes external, criteria, which are of no material importance.

3. In the papers under discussion, the choice of these criteria and their application resulted in the adopted classifications failing to allow for or to reflect the actual nature of the phenomena involved.

4. What has been asserted indicates that the time is ripe for establishing a new classification of the reactions occurring in mixtures of solid substances.

5. The recommended principle underlying the classification of these reactions provides for their subdivision into three major classes:

I. Those limited by chemical reaction.
II. Those limited by diffusion.
III. Those limited by evaporation and sublimation.

Class I of this listing comprises many processes in which the part played by physical phenomena is unimportant, owing to the low velocity of the chemical reaction proper, the negligible thickness of the diffusion layer, the high diffusion coefficients, and similar factors.

Class II comprises most of the so-called solid-phase processes involving the formation of a fairly substantial diffusion layer of the reaction product upon the particles of some reagent.

Class III comprises some processes in which spinels, sulfides, and other compounds are formed, which are limited by the evaporation or sublimation of some substance.

6. This principle enables us to classify all solid-phase reactions that are of any practical importance. This principle, together with its further development, makes it possible to generalize and discriminate among "solid-phase" reactions in accordance with basic criteria that govern their kinetic behavior.

7. A single chemical transformation occurring in a mixture of solid substances may come under the heading of different classes of the recommended classification system during various stages of the process, if the relative values of the individual resistances to the transformation change appreciably during the course of the process.

LITERATURE CITED

[1] S.Z.Roginsky, J. Phys. Chem. USSR, 12, 4 , 427 (1938).

[2] W.Jander, Z. angew. Chem., 41, 73 (1928).

[3] W.Muller, Chem. Fabrik., 32, 333 (1933).

[4] A.N.Volsky. Theory of Metallurgical Processes. (1935).

[5] S.T.Rostovtsev. Theory of Metallurgical Processes. (1945).

[6] W. Jost. Diffusion und chemiche Reaktion in festen Stoffen (1937).

[7] W.Garner, Prog. Chem., 8, 8, 1173 (1939).

[8] W.Garner, Science Progress, 33, 130, 209 (1938).

[9] G.Hüttig. Kolloid-Z. 94. H.2, 137 (1941); H 3, 258 (1941).

[10] A.M.Ginstling and B.I.Brounshtein, J.Appl. Chem. 23, 12 (1950).

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THE RELATIVE VELOCITY OF DROPS IN THE TRANSITIONAL REGION*

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In our preceding report [1] we put forward the hypothesis that, as in the laws governing the motion of a solid sphere in a liquid, in the case of a drop moving in a liquid medium there must be a region, defined by values of the Reynolds number lying between 190 and 1.2, in which the relative velocities of the drops will be proportional to their diameter. It is evident that in this case the variables defining the relative drop velocity will be the same as before, when the Reynolds numbers were higher than 190, i.e., the variables will be:

$\underline{w} = w_d + w_m$, the relative velocity of the drop, meters/sec; w_d, the velocity of the drop with respect to the wall of the container, meters/sec; w_m, the velocity of the medium, meters/sec.; γ_d, the specific gravity of the substance in the drop, kg/m^3; γ_m, the specific gravity of the medium, kg/m^3; μ_d, the viscosity of the substance in the drop, kg·sec/m^2; μ_m, the viscosity of the medium, kg·sec/m^2; $\underline{d}$, the drop diameter, meters, assuming its shape is rigorously spherical; $\underline{D}$, the diameter of the container, meters; and g, the acceleration of gravity, meters/sec^2.

As before, these variables will be related together by the following criterial equation:

$$\underline{f}\left(Re, Ar, \frac{\mu_d}{\mu_m}, G, \frac{\gamma_m - \gamma_d}{\gamma_d}\right) = 0 \qquad (1)$$

It is the purpose of the present paper to establish the form of this equation.

EXPERIMENTAL

The value of the Reynolds number in Equation (1) is found from the equation:

$$Re = \frac{dw\gamma_m}{\mu_m g}.$$

*Report III of a series on the motion of a body within a medium.

If the value of the Reynolds number is to be below 190, we must either have drops of small diameter, which therefore move at low velocity, or use a high-viscosity medium. We were not very successful in producing drops of small diameter (less than 1-1.5 mm) by slowly emitting a liquid from a capillary tube. Even the finest capillary tubes, specially prepared by drawing out glass tubing in a Bunsen burner flame, produced drops of fairly large diameter. The reason for this was the uneven, sawtooth tip of the capillary, as was always observed to be the case under a magnifying glass.

We therefore had to resort to the use of a medium with high viscosity for observing the motion of drops in the transitional region. The high-viscosity medium employed was an aqueous solution of sugar. In our tests we used solutions of approximately 20 and 40% strengths. The specific gravities of these two solutions were determined in specific gravity bottles at 5.3, 13.8, and 20°, their viscosity being determined at the same temperatures in an Engler viscosimeter, using water as the standard solution.

The values of specific gravity in the 5.3-20° range lay upon a straight line in the specific gravity - temperature diagram; we therefore expressed them in the form of empirical equations. The equation for a 20% solution was:

$$\gamma_m = 1108.36 - 0.85\ t,$$

while that for a 40% solution was:

$$\gamma_m = 1186.59 - 0.515\ t.$$

These equations were used to compute the specific gravities in our working up of the experimental results.

The viscosity values found for these three temperatures did not lie on a straight line in the viscosity - temperature diagram; we therefore found the values of the viscosity at any temperature by means of graphical interpolation when working up our experimental results.

All the substances employed in our research were previously distilled. The following fractions were collected at atmospheric pressure: 111° toluene; 183° aniline; 193-194° dimethylaniline; 80° benzene; and 73.5-74° carbon tetrachloride. Glass columns 15 mm in inside diameter and 0.8 and 1.5 meters high were constructed so that the motion of the drops could be observed. The design of the columns differed, depending upon whether the drops of the tested substance floated or sank in the given medium. The design of the columns has been described in detail in one of our previous reports [1].

All the experiments in the present research were performed in a motionless medium. The motion or stationary state of the medium is of no importance in a study of the relative velocity of drops.

The table shows the experimental conditions and the test results. Besides our own experiments, we have also listed and worked up the experiments made by Allen [2] on the motion of air bubbles in water and in aniline. Allen's experiments were performed in a column with an internal diameter of 35 mm. Allen's experiments have not been worked up as yet in a criterial form.

All the experimental data were worked up by calculating the values of all the criteria and simplexes entering into Equation (1). We have already cited the equation for calculating the Reynolds number; it is based upon a calculation of the physical properties of the medium. Archimedes' criterion was calculated from the physical properties of the substance, i.e., from the equation:

Experiment No.	Temp. °C	Drop diameter $d \cdot 10^3$, meters	Drop velocity w, m/sec	Specific gravity of the substance γ_s (kg/m^3)	Specific gravity of the medium γ_m (kg/m^3)	Viscosity of the substance $\mu \cdot 10^4$, kg-sec/m^2	Viscosity of the medium $\mu \cdot 10^4$, kg-sec/m^2	Reynold's number: Observed	Reynold's number: Calculated	Discrepancy %
Drops of nitrobenzene in sugar solution										
1	16	2.673	0.0557	1207.18	1094.78	2.2320	2.0560	80.83	82.21	+ 1.7
2		2.759	0.0562					84.16	88.51	+ 5.2
3		2.532	0 0489					67.22	72.51	+ 7.9
4		2.102	0.0446					51.37	46.20	-10.1
5	18	1.420	0 0265	1205.20	1093.06	2.1305	1.9472	21.04	19.53	- 7.1
6		1.420	0.0272					21.62	19.53	- 9.7
Drops of carbon tetrachloride in sugar solution										
7	18.5	1.789	0.0888	1596.96	1092.63	1.0122	1.8544	90.55	78.05	-16.0
8		1.721	0 .0811					79.52	71.30	-10.3
Drops of aniline in water										
9	20	3.676	0.0375	1021.64	998.23	4.5148	1.0282	136.4	141.6	+ 3.8
10		3.745	0. 0375					139.0	147.9	+ 6.4
11		3.169	0.0305					95.7	100.2	+ 4.8
Drops of water in benzene										
12	21	1.928	0.0625	998.02	877.70	1.0030	0.6400	166.2	158.3	- 4.8
Drops of water in dimethylaniline										
13	21	2.048	0.0238	998.02	955.40	1.0030	1.4230	33.36	38.05	+14.1
14		2.190	0.0261					39.11	44.49	+13.7
Drops of water in toluene										
15	20	2.299	0.0784	998.23	865.80	1.0282	0.5912	269.1	276.2	+ 2.7
16		2.289	0.0784					267.9	273.4	+ 2.0
17		1.789	0.0642					171.5	153.8	-10.3
18		1.789	0.0637					170.2	153.8	- 9.6
19		1.684	0.0443					111.4	114.6	+ 2.9
Drops of benzene in sugar solution										
20	21	1.903	0.0478	877.70	1090.50	0.6400	1.7951	56.34	56.64	+ 0.5
21		2.035	0.0476					60.00	66.23	+10.4
22		1.911	0.0408					48.28	57.19	+12.8
23	16	2.048	0.0408	833.01	1178.35	0.6897	6.0160	16.60	18.00	+ 8.4
24		2.048	0.0415					16.89	18.00	+ 6.6
25		2.121	0.0435					18.50	19.54	+ 5.6
26		2.373	0.0489					23.06	25.38	+10.1

Experiment No.	Temp. °C	Drop diameter d·10³, meters	Drop velocity v, meters/sec	Specific gravity of the substance γ_s (kg/m³)	Specific gravity of the medium γ_m (kg/m³)	Viscosity of the substance μ·10⁴, kg-sec/m²	Viscosity of the medium μ·10⁴, kg-sec/m²	Reynold's number observed	Reynold's number calculated	Discrepancy %
				Drops of dimethylaniline in sugar solution						
27	-	2.254	0.0395	955.40	1050.50	1.4230	1.7851	55.15	60.12	+ 9.0
28	21	2.291	0.0405					57.47	61.03	+ 6.2
29		2.552	0.0464					73.32	80.33	+ 9.6
30		2.291	0.0344					15.66	17.64	+12.7
31	16	2.628	0.0421	959.40	1178.35	1.5418	6.0460	21.98	25.44	+15.7
32		2.392	0.0395					18.77	20.43	+ 9.9
				Drops of toluene in sugar solution						
33		1.684	0.0410					40.56	41.48	+ 2.2
34		1.495	0.0393					34.52	31.09	- 9.9
35	19	1.495	0.0387	866.60	1092.21	0.6122	1.8951	33.99	31.09	- 8.5
36		1.958	0.0533					61.30	58.97	- 3.8
37	20	1.337	0.0276	865.80	1176.29	0.5912	5.0304	8.80	8.86	+ 0.7
38		1.969	0.0455					21.36	21.86	+ 2.4
				Air bubbles in water						
39		0.218	0.0145					2.39	2.40	+ 0.4
40	8.5	0.282	0.0203					4.18	4.37	+ 4.5
41	8.6	0.283	0.0218	1.25	999.84	0.0179	1.3937	5.59	4.74	+ 3.3
42	8.4	0.310	0.0236					5.35	5.46	+ 2.1
43	7.6	0.340	0.0267	1.26	999.90		1.4355	6.44	6.74	+ 4.7
44		0.374	0.0313					8.55	8.46	+ 1.1
45	8.4	0.380	0.0320					8.88	8.78	- 1.1
46	8.3	0.402	0.0339	1.25	999.84		1.3937	9.96	10.01	+ 0.5
47		0.412	0.0335					10.69	10.60	- 0.9
48	8.4	0.448	0.0389					12.73	12.91	+ 1.4
49	7.9	0.482	0.0423					15.50	15.25	+ 5.2
50	7.8	0.610	0.0554	1.26	999.90	0.0179	1.4355	24.03	26.43	+10.0
				Air bubbles in aniline						
51	10.0	0.574	0.0229	1.244	1030.29		6.6127	2.09	2.21	+ 5.9
52	11.8	0.660	0.0300					3.39	3.28	- 3.3
53	11.8	0.690	0.0309	1.239	1028.56		6.1160	3.66	4.24	+16.1
54	11.0	0.702	0.0343	1.243	1029.40		6.3710	4.00	3.76	- 5.1
55	10.0	0.748	0.0343	1.244	1030.29		6.6127	4.07	2.09	+ 0.5
56	12.0	1.070	0.0600					11.00	8.69	-21.0
57	11.8	1.078	0.0643	1.239	1028.56		6.1160	11.88	10.31	-13.1
58	12.0	1.104	0.0690					11.36	10.90	- 4.1

$$Ar = \frac{d^3 \gamma_d^2}{\mu_d^2 g} \frac{\gamma_m - \gamma_d}{\gamma_d},$$

and the criterion of geometrical similarity from the ratio:

$$G = \frac{d + D}{D}.$$

We found that in our experiments the relationship between all the similarity criteria and simplexes entering into Equation (1) may be expressed as follows):

$$Re = \left[0.24 + 0.008 \left(\frac{\gamma_m - \gamma_d}{\gamma_d}\right)^{0.2}\right] Ar^{2/3} \left(\frac{\mu_d}{\mu_m}\right)^{4/3} G^{-1} \qquad (2)$$

or

$$Re = a\, Ar^{2/3} \left(\frac{\mu_d}{\mu_m}\right)^{4/3} G^{-1}. \qquad (2a)$$

Evaluation of Results

Substituting the appropriate expressions in Equation (2a) for the criterion and simplex symbols and making all the necessary reductions, we get:

$$w = ad \frac{\gamma_d^{2/3} (\gamma_m - \gamma_d)^{2/3}}{\gamma_m} \frac{g^{2/3}}{\mu_m^{1/3}} G^{-1}. \qquad (3)$$

This shows that the relative velocity of drops is directly proportional to their diameter in geometrically congruent systems throughout the range of Reynolds numbers investigated by us (10-270). Thus, the motion of a drop in a liquid medium resembles that of a solid sphere. As we know [3], the velocity of a solid sphere in a liquid is likewise proportional to its diameter at Reynolds numbers ranging from 30 to 300.

At very low Reynolds numbers (below 1.2), the drop velocity is directly proportional to the square of its diameter. The relationship of the quantities that determine velocity in this region has not yet been worked out in criterial form. Finding this equation will be the subject of our next research.

It also follows from Equation (3) that the relative velocity of a drop in the transitional region is wholly independent of the viscosity of the substance constituting the drop, depending solely upon the viscosity of the medium. Thus, the viscosity of the drop substance may be eliminated from the equations for computing the values of the criteria and simplexes entering into Equation (1). The viscosity of the substance can be excluded from the value of the Archimedes number by calculating the latter from the physical properties of the medium, i.e., by using the equation:

$$Ar = \frac{d^3 \gamma_m^2}{\mu_m^2 g} \frac{\gamma_m - \gamma_d}{\gamma_d}.$$

With the elimination of the substance's viscosity, the number of variables governing the motion of the drop is reduced to one. Hence, the number of criteria and simplexes entering into Equation (1) must likewise be reduced to one. This reduction must be effected by eliminating the viscosity simplexes.

Working up the experimental data with the new equation for the Archimedes number and with the viscosity simplexes eliminated yields a new criterial equation for the motion of a drop in a liquid medium in the transitional region, namely:

$$Re = \left[0.41 - 0.105\left(\frac{\gamma_m - \gamma_d}{\gamma_d}\right)^{0.2}\right] Ar^{2/3}\left(\frac{d}{D}\right)^{1/3} \qquad (4)$$

or

$$Re = b\, Ar^{2/3}\, G. \qquad (4a)$$

Equation (4) yields much better agreement between the experimental and the computed values of the Reynolds number than does Equation (2). The Reynolds numbers computed from Equation (4) are listed in the next to the last column of the table for all the experiments. The last column gives the discrepancy between the computed and observed values. With but few exceptions, the convergence is quite satisfactory.

Equation (4) can also be employed to determine the motion of the drop itself in a moving medium [4]. Equation (4) may be written as follows:

$$\frac{\underline{d}w\gamma_m}{\mu_m g} = \frac{d(w_d + w_m)\gamma_m}{\mu_m g} = b\, Ar^{2/3}\, G$$

or

$$\frac{dw_d\gamma_m}{\mu_m g} + \frac{dw_m\gamma_m}{\mu_m g} = b\, Ar^{2/3}\, G$$

or

$$Re_d + Re_m = b\, Ar^{2/3}\, G. \qquad (5)$$

From this equation it is easy to establish the instant of arrest, i.e., the time when the motion of the drop becomes zero, owing to the high velocity of the medium. At $\underline{w}_d = 0$, $Re_d = 0$. Hence the instant of arrest is defined as the attainment of the following equality:

$$Re_m = b\, Ar^{2/3}\, G. \qquad (6).$$

All the equations cited above apply only to systems in which there is no mass exchange between the drops and the medium or this mass exchange is slight. When mass exchange exists, Equations (1-6) require the introduction of supplementary, new criteria. The motion of drops under mass-exchange conditions is the subject of our future investigation.

The factors $\underline{a}$ and $\underline{b}$ in the equations cited above are constants for any system, depending solely upon the value of the Archimedes simplex. These factors allow for the direction of motion of the drop and the departure of its form from the strictly spherical. It should be noted that similar constants were found in the region of turbulent motion, defined by Reynolds numbers ranging from 190 to 1000, which have been investigated by us previously [1]. Their values are much more dependent, however, upon the value of the Archimedes simplex than in the present case. It follows, therefore, that in the transitional region the resistance due to the departure of the drop's form from the strictly spherical, resulting from the direction of its motion rather than from deformation caused by the differences between the specific gravities of the medium and the drop's substance, is much more important.

SUMMARY

1. Two forms of the criterial equations defining the relative velocity of drops

in a liquid medium have been derived for Reynolds numbers ranging from 2 to 270 and with no mass exchange between the drops and the medium present.

2. It has been shown that the velocity of the drop is directly proportional to its diameter in the investigated (transitional) region.

3. It has been shown that the velocity of the drop in the transitional region is independent of the viscosity of the substance constituting the drop, being governed solely by the viscosity of the medium.

4. In the criterial equations describing the drop motion, a factor has been isolated that makes special allowance for the departure of the drop's form from the strictly spherical.

5. An equation has been derived for determining the velocity of the drop proper in the transitional region.

6. An equation has been derived for determining the instant at which motion stops in the transitional region.

LITERATURE CITED

[1] M.I.Smirnov and V.L.Ruban, J. Appl. Chem. 22, 1068 (1949).

[2] H.S.Allen, Phil. Mag. (SV), L, 323, 519 (1900).

[3] P.G.Romankov. Hydraulic Processes in Chemical Technology. State Chemical Press (1948).

[4] M.I.Smirnov and V.L.Ruban, J. Appl. Chem. 22, 1211 (1949).

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FLOW THROUGH A LAYER OF SOLID PARTICLES •

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In previous reports [1,2], one of the present authors, together with V.L.Ruban, found the criterial equations that define the motion of drops in a medium. Moreover, another report [3] specified the conditions of arrest in extraction columns, i.e., the conditions under which the velocity of the drops against the liquid counterflow becomes zero. All of these equations may serve as a basis for the analysis of the interesting phenomenon of the formation of a suspension layer of liquid and solid particles in the current.

The phenomenon of a suspension layer consists of the following. When a liquid or a gas rises through a layer of free-flowing material, the height of the layer of free-flowing material begins to increase at a certain velocity of flow, owing to an increase in the distance between the individual particles. A certain increase in height of the layer of free-flowing material will correspond to each velocity of the medium. The higher the flow velocity, the more will the height of the layer be and the higher will the top level of the particles suspended in the current be.

The suspended particles are in continuous motion, but the level of the suspended layer remains practically constant, provided the flow velocity does not change and provided bubbles of the medium do not break through the layer instead of the medium moving along smoothly. This sort of breakthrough is observed in tubes of small diameter when a certain velocity of the medium is reached. This picture of the suspension layer enables us to consider the suspended particles as motionless, with all the motion referred to the medium.

It is obvious that a medium whose motion produces the phenomenon of the suspended layer loses some of its head in passing through a layer of solid material. The greater the initial height of the layer of solid material and the degree to which its height is increased, as well as the higher the velocity of the medium, the greater the loss of head. The phenomenon of the suspension layer develops into a transport movement when the velocity of the medium is sufficiently high; the particles of the free-flowing material are then carried along by the moving medium, and are no longer suspended in the current at a certain height.

Parent [4], Wilhelm [5], Leva [6], and several other investigators have tried

• Report IV of a series on the motion of a body within a medium.

to establish the relationship between the different variables that govern the phenomenon of the suspension layer. But all the efforts of these authors met with failure. Up to the present time we have no general equations to describe the phenomenon of the suspension layer that would enable one to determine the characteristics of the phenomenon under given conditions.

Observation of the phenomenon of the suspended layer and critical examination lead us to conclude that this phenomenon can be described as a functional relationship between such variables as the velocity of the medium, the specific gravity of the medium, the specific gravity of the substance in suspension, the viscosity of the medium, the loss of head, the dimensions of the suspended particles, the diameter of the apparatus, the initial height of the layer of solid particles, the height of the suspended particles, and acceleration due to gravity. Thus, a description of the phenomenon requires a minimum of ten variables.

We shall adopt the following notation and the following dimensions of these variables: w is the velocity of the medium, meters/sec; γ_m is the specific gravity of the medium, kg/m^3; γ_d is the specific gravity of the substance in suspension, kg/m^3; μ is the viscosity of the medium, kg·sec/m^2; Δp is the loss of head, kg/m^2; d is the governing dimension of the particles in suspension, meters; D is the diameter of the column, meters; h_0 is the initial height of the layer of solid particles, meters; h is the height of the layer in suspension, meters, and g is the acceleration of gravity, meters/sec^2.

Thus, all the ten variables are expressed in three units of measurement. According to the π-theorem of the theory of dimensions, the relationship of all the variables listed above must therefore be determined by seven similarity criteria and simplexes.

In order to establish the relationship of all the variables, we consider the phenomenon of a suspension layer as a complex phenomenon, consisting of at least three superposed processes. The first process is the flow of the liquid or the gas through a tube filled to some extent or other with free-flowing material. The second process is the increase in the height of the layer as the result of the increased distance between the individual particles. Lastly, the third process is the maintenance of the top level of the raised layer at the height it has reached.

We describe the first process by means of Romankov's proposition [7]; on the basis of a critical review of the pertinent researches he concluded that the generalized equation for the flow of a liquid or a gas through the layer is as follows:

$$Eu = CRe^{u}G_1^{p}G_2^{r}, \qquad (1)$$

where C is a dimensionless coefficient; G_1 is the first criterion of geometrical similarity, equal, say to d/D; and G_2 is the second criterion of geometrical similarity, equal, say, to h_0/D; the values of the exponents n, p, and r depend upon the nature of the flow, i.e., upon the value of the Reynolds number.

Zhavoronkov [8] writes Equation (1) as follows:

$$Eu = 200\ Re^{-1}\ G_1,$$

for laminar flow (for $Re \leqslant 50$-60) and systems with identical values of G_2;

$$Eu = 7.6\ Re^{-0.2}\ G_1,$$

for turbulent flow, with Reynolds numbers of from 60 to 7000; and

$$Eu = 1.3\ G_1,$$

for turbulent flow with Reynolds numbers above 7000.

According to Zhavoronkov, therefore, the transition from laminar to turbulent flow takes place at Reynolds numbers of 50 to 60 for a current passing through a layer. Other authors give different figures for the critical value of the Reynolds number. Fedorov [8], for instance, found that the transition from laminar to turbulent flow occurs at a Reynolds number of 7 for a layer consisting of small balls.

In working up our experimental data on the phenomenon of a suspension layer consisting of tiny balls, we also found that the best agreement of the calculated values of the Euler number with the observed values is obtained when the point of transition between laminar and turbulent flow is taken to lie at a Reynolds number of 7, as will be shown in our subsequent reports. In general our experiments were carried out at Reynolds numbers that exceeded 7 and were lower than 7000. We therefore used the following equation:

$$Eu = C_1 Re^{0.2} G_1^{p}, \qquad (2)$$

to describe the first elementary process involved in the phenomenon of the suspension layer. The values of the criteria in Equation (2) were calculated from the following ratios:

$$Eu = \frac{\Delta p g}{\gamma_m w^2},$$

$$Re = \frac{dw\gamma_m}{\mu g},$$

$$G_1 = \frac{d}{D}.$$

The second elementary process involved in the phenomenon of the suspension layer is the increase in the height of the layer from its initial value h_0 to the final value h. As we stated earlier, we have derived criterional equations defining the motion of drops in a medium. For the turbulent region, this equation is:

$$Re = \left[1.4 - 0.257 \left(\frac{\gamma_m - \gamma_s}{\gamma_s} - 0.13\right)^{0.248}\right] Ar^{0.5} G \qquad (3)$$

and for the transitional region:

$$Re = \left[0.41 - 0.105 \left(\frac{\gamma_m - \gamma_s}{\gamma_s}\right)^{0.2}\right] Ar^{2/3} \left(\frac{d}{D}\right)^{1/3}. \qquad (4)$$

The structure of these equations is identical, except for the expression for the criterion of geometrical similarity. In Equation (3) the criterion of geometrical similarity is computed from the ratio $\frac{d + D}{D}$, while in Equation (4) it is computed from the ratio d/D. In subsequent reports we shall have the opportunity of showing that Equation (3) can also be expressed in a notation similar to that employed for Equation (4), i.e., as:

$$Re = \left[a - b \left(\frac{\gamma_m - \gamma_s}{\gamma_s} - C\right)^{m}\right] Ar^{0.5} \left(\frac{h_0}{D}\right)^{1/3}. \qquad (3a)$$

The expressions within the Brackets in Equations (3), (4), and (3a) allow for departures of the form of the drops from the strictly spherical and for the direction

of the drops's motion. It is evident that these equations are also applicable to spherical balls, but in this case the expressions within the brackets become constants, inasmuch as the balls in the suspension layer may be considered motionless and their form is strictly spherical. We may then write:

$$Re = C_2 Ar^{0.5} G_2^{1/3}. \qquad (3b)$$

to describe the second elementary process involved in the phenomenon of the suspension layer when it occurs in the turbulence region. The value of the Reynolds number is computed as before, while the value of the Archimedes number is computed from:

$$Ar = Ga \frac{m - s}{m} = \frac{d^3 s^2}{\mu^2} \cdot \frac{s - m}{m}.$$

The third elementary process involved in the phenomenon of the suspension layer is the process of maintaining the expanded layer at the height it has attained, i.e., a process that is wholly similar to "arrest" in extraction columns. As we know [3], a process of this sort is described by the same Equations (3), (3a), and (3b), with the sole exception that the criterion G_3, calculated from the ratio:

$$G_3 = \frac{h}{D},$$

must be substituted for the criterion $G_2 = h_0/D$ in these equations. The equation for the third elementary process will then be:

$$Re = C_3 Ar^{0.5} G_3^{1/3}. \qquad (4)$$

In this equation the criterion G_3 denotes the ratio of the level reached when the layer's height is raised to the diameter of the apparatus.

Representing the whole phenomenon of the suspension layer as a combination of these three elementary processes enables us to describe it by means of a single equation, constituting the product of the three equations (2), (3b), and (4), we have derived for the separate elementary processes. This is legitimate, since it was assumed that the criterial equations are the products of the criteria in one degree or another. Thus, we multiply and rearrange these equations suitably and get a criterial equation that describes the phenomenon of the suspension layer at Reynolds numbers ranging from 7 to 7000 as follows:

$$Eu = CRe^{-2.2} Ar G_1^{p} G_2^{1/3} G_3^{1/3}. \qquad (5)$$

Equation (5) contains 7 criteria and similarity simplexes, inasmuch as the Archimedes criterion is a product of the Archimedes simplex and the Galileo criterion. Thus it is evident that Equation (5) satisfies the requirements of the π-theorem. It is obvious that a similar equation can be derived for laminar flow.

The only unknowns in Equation (5) are the exponent of G_1, the first criterion of geometric similarity, and the coefficient C. We had to perform numerous experiments with lead and glass balls, suspended in currents of water, kerosene, air, and carbon tetrachloride, to find these unknowns. Working up the data of these experiments enabled us to find the final form of Equation (5), namely:

$$Eu = 8.58\, Re^{-2.2}\, Ar G_1^{0.5} G_2^{0.33} G_3^{0.33}. \qquad (6)$$

Moreover, the experiments we ran with solid particles of regular, though not spherical, form make it possible to extend Equation (5) to the formation of a suspension layer consisting of particles of any form. The conditions under which all these experiments were run, and a discussion of their results, will be set forth in our subsequent reports.

SUMMARY

1. The phenomenon of the suspension layer has been analyzed as a complex phenomenon, consisting of three elementary processes: the flow through the layer of free-flowing material; the increase in the height of the layer of free-flowing material as the result of the increase in the distance between the individual particles; and the maintenance of the heightened layer at the level it has reached.

2. The corresponding criterial equation has been found for each elementary process on the assumption that the particles of free-flowing material are strictly spherical.

3. A general equation has been derived, describing the phenomenon of the suspension layer as a whole, as the product of the equations for the separate elementary processes. The unknowns in the equation: the coefficient and the exponent of one of the criteria, have been found from experimental data.

4. Methods are outlined for applying this criterial equation to all cases in which a layer consisting of particles of any form is in suspension.

LITERATURE CITED

[1] N.I.Smirnov and V.L.Ruban., J. Appl. Chem. 22, 1068 (1949).

[2] N.I.Smirnov and V.L.Ruban, J. Appl. Chem. 24, No. 1, (1951).

[3] N.I.Smirnov and V.L.Ruban, J. Appl. Chem. 22, 1211 (1949).

[4] I.Parent, N.Vogel, C. Steener, Chem.Eng.Prog., 43, 429 (1947).

[5] R.Wilhelm, M.Kwauk, Chem. Eng. Prog., 44, 201 (1948).

[6] M.Leva and co-workers. Chem. Eng. Prog., 43, 549 (1947); 44, 511, 619 (1948).

[7] P.G.Romankov. Hydraulic Processes in Chemical Technology. State Chemical Press (1948).

[8] N.M.Zhavoronkov. Hydraulic Principles of the Scrubber Process. Contemporary Science. (1944).

[9] I.M.Fedorov, Symposium: Contemporary Problems of the Drying Process. State Power Press (1941).

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AN INVESTIGATION OF THE PASSIVATION OF IRON IN THE HNO_3-H_2SO_4-H_2O SYSTEM

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The HNO_3 – H_2SO_4 – H_2O system is used technologically as a nitrating mixture. It possesses a complex ionic and molecular structure [1-13]. Its oxidative properties, its conductivity, and its other properties vary widely. There is no doubt of the considerable importance of an investigation of the passivation of iron in the HNO_3 – H_2SO_4 – H_2O system.

The compositions of mixtures of nitric acid, sulfuric acid, and water in which iron is passivated are specified in the paper by Krestovnikov and Klinov [14]. Ivanova has obtained comparative data on the corrosion and passivation of iron in the liquid and gas phases [15]. The region of the passive and intermediate (periodic) states of iron in nitric acid solutions is set forth in the paper by Golombik, Levina, and Pein [16]. Akimov and Batrakov have measured the potential of iron in solutions of nitric acid [17].

The common causes of the passivity of metals in oxidizing media may be [18]: the formation of a protective film [19,20], the formation of an adsorbed-oxygen layer or of a surface compound [21-27], or the formation of a highly stable modification of the metal in its surface layer. It is supposed that a film of the trivalent [28a, 29, 30a] and the sexivalent [31] oxides of the metal is formed on iron in concentrated nitric acid, as well as a surface monomolecular oxide that has an extremely high oxygen pressure, compared to ordinary iron oxide [27]. The protective oxygen film is formed by the interaction of the iron with the oxygen in the undissociated molecules of nitric acid [32] and by the direct oxidation of the metal by nitrogen dioxide [29]. The passivity of iron in sulfuric acid in the presence of anodic polarization is the result of its surface being coated with a ferrous sulfate [29,30b] or ferric sulfate [30a]. When a mixture of nitric and sulfuric acids contains a high percentage of the latter, the surface of the metal immersed therein becomes coated with ferric sulfate [28b].

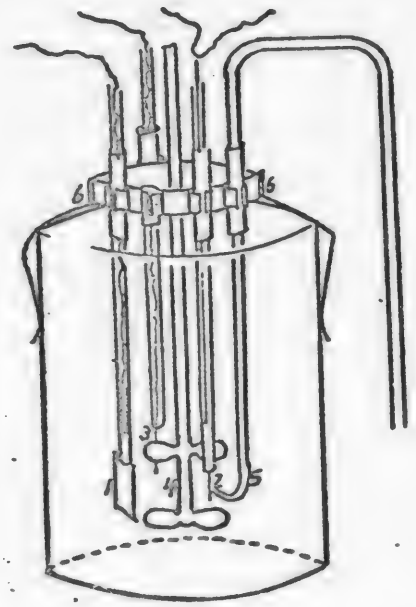
Small percentages of sulfuric acid added to nitric acid interfere with the passivation of iron, while high percentages promote it [28a].

EXPERIMENTAL

Research method. In our experimental investigations, we determined: the corrosion rate of the iron, its potential during the period of corrosion, the ultimate

cathode current density at a platinum electrode, and the ultimate anode current density at the iron electrode.

In our measurements of the corrosion rate and the potential (cf drawing), two samples of Armco iron* were placed in a certain place (which was always the same) in a 1-liter reaction beaker. The samples, shaped like tiny spades 2 x 1.5 x 0.5 cm in size mounted on rods with a rubber packing in glass tubes, were held fast in the bushings of the metallic electrode holder. The beaker was kept in a fixed position by means of a metal ring attached to a stand. A stirrer, attached to the same stand, passed through the center of the electrode-holder ring and was always immersed to the same depth. One of the bushings of the electrode holder held a siphon for a liquid connection to the comparison electrode. The latter consisted of a saturated calomel electrode, which was mounted on the same stand at the level of the reaction medium in the beaker.



Apparatus for determining corrosion and electrode polarization.

1-Iron sample subjected to natural corrosion 2-Measuring platinum cathode or iron anode 3-Auxiliary platinum anode or cathode. 4-Mechanical stirrer 5-Siphon for liquid connection to comparison electrode 6-Electrode holder

A large quantity (500 cm^3) of the reaction medium was used in order to eliminate any noticeable change in concentration as the result of corrosion. In most cases, the tests lasted 10-40 minutes, though in slightly corrosive media they lasted 2 hours. The tests were made with vigorous stirring (650 rpm of the stirrer). The rate of corrosion was determined by the sample's loss of weight and size during the period of corrosion.

The same apparatus was used to determine the ultimate electrode current densities under the same conditions as those under which corrosion was studied.

The platinum cathode was a smooth wire 1 cm long and 0.05 cm in diameter. The ultimate cathode current density, at which the potential drops sharply as the current in the circuit is gradually increased or at which it rises sharply as the current is diminished, was found from the curves of cathodic polarization. Moreover, we made several determinations in every reaction medium by observing the sharp rise or fall of the current as the potential fell or rose.

The ultimate anode current density, at which the current in the circuit drops sharply and the electrode potential rises sharply, was determined at a sheared-off iron wire covered with nitro-lacquer, at a bare iron wire 1 cm long, and, in some instances, at a platinum wire sealed into a glass tube. The diameter of the iron

*The iron used in this research contained: 0.05% carbon, 0.03% manganese; 0.018% phosphorus, and less than 0.01% silicon.

and platinum wires was 0.05 cm.

The ultimate anode current density at the sheared-off wire was measured by observing the sharp drop of the current in the circuit or its reaching a maximum value, which occurred at a certain instant when it was gradually increased by diminishing an external resistance in the circuit. With the iron wire, the ultimate anode current-density was determined by the sharp rise in the potential paralleled by a drop in the current; in this case, in contrast to determinations made at the sheared-off section, the current continued to rise in most cases as the circuit resistance was decreased, even after the ultimate current density had been reached.

Thus, the wire measured the initial passivation, which takes place without any loss in electrode conductivity, whereas the sheared-off section measured the passivation caused by the loss, or the extremely great diminution, of electrode conductivity.

All measurements were made in a water thermostat at a temperature of 25.5 ± 0.5°.

State of the reaction mixtures. Some of the important indexes of the state of the reaction mixtures, derived from the references in the literature, are listed in Table 1.

The percentages of homopolar HO_2OH molecules in the mixture, based on the total nitric acid present, were found from data on the degree of dehydration of homopolar nitric acid in extremely highly concentrated mixtures of nitric and sulfuric acids and on the degree of dissociation of homopolar molecules into ions in aqueous solutions of nitric acid [7]. This was done by drawing a line through a point on the straight line representing the composition of nitric acid - water mixtures in the triangular diagram of the ternary $HNO_3 - H_2SO_4 - H_2O$ system that is parallel to the line representing the state of nitric acid in ternary mixtures in which the acid consists of nothing but homopolar molecules. On the assumption that there is a definite parallelism between hydrating and dissociating properties, the degree of dissociation of the homopolar molecules equal to their dissociation in aqueous solutions of nitric acid was attributed to these lines. In the thus extrapolated triangular diagram we found the homopolar molecules as percentages of the total nitric acid in the investigated mixtures, and from these figures the absolute content of homopolar molecules.

The percentage of nitric acid vapor in the vapor above ternary and binary mixtures and the boiling points of the latter were determined from diagrams given in the literature [33] for two pressures: 760 and 350 mm of mercury. The partial pressure of nitric acid vapor at the constant temperature of 120° was calculated from these figures, using the Clausius-Clapeyron equation.

It should be noted that the lower heats of evaporation were used in our calculations for mixtures containing a high percentage of sulfuric acid. Hence, the relative rise of the vapor tension of nitric acid as the concentration of sulfuric acid rises must be sharper than the change in the true concentration of homopolar nitric-acid in the liquid.

Lastly, the heats of formation of the test mixtures were found from the general diagram for the heats of formation of ternary mixtures, [34].

Experimental data. The data obtained in our experimental investigation are summarized in Table 2. The notation used is as follows: C_a is the rate of corrosion; E_{Fe} is the potential of the dissolving metal as against a saturated calomel electrode; I_{cb} and I_{ca} are the ultimate cathode current densities at which the potential drops sharply when the current is gradually increased; I_{cb} is the current befor the potential drop; I_{ca} is the current density after the potential drop; I'_{cb}

and I'_{ca} are the ultimate cathode current densities at which the potential rises sharply when the current is gradually decreased; I'_{cb} before the potential rise; I'_{ca} after the potential rise; I_{ab} is the ultimate (maximum) anode current density before it drops sharply or before the potential rises; and I_{aa} is the current density after it drops or after the potential rises.

The mixtures are arranged as follows in Tables 1 and 2. The aggregate acid concentration and the ratio of the sulfuric acid concentration to that of the nitric acid increase in groups of six: Nos. 1-6, 7-12, 13-18, 19-24, and 25-30, from the first mixture to the last. Mixtures Nos. 1, 7, 13, 19, and 25; 2, 8, 14, 20, and 26, and so forth, i.e., mixtures with the same ordinal number within a group of six, have the same ratio of sulfuric acid to nitric acid concentrations. The acid concentration in these mixtures diminishes as we proceed downward in the series.

The tested mixtures may be divided into three groups as far as their corrosion activity is concerned: 1) passivating mixtures; 2) mixtures causing an active form of corrosion; and 3) mixtures with an intermediate form of corrosion activity. Mixtures 1-5, 9, and 10 are passivating mixtures. The second of these mixtures inhibits and produces extremely active corrosion simultaneously, however, while Mixture No. 10 exhibits unstable passivity, as may be seen from the magnitude and the fluctuation of the metal's potential during corrosion. Mixtures 13, 14, and 19-30 cause active corrosion. Mixtures 7, 8, 11, and 15-17 produce an intermediate form of corrosion, weaker than active corrosion. This may be shown by comparing the potential and rate of corrosion of iron in such mixtures with the potential and rate of corrosion of iron in actively corroding mixtures that possess an identical ratio of acid concentrations. At lower corrosion rates, the potential of corroding iron in Mixtures 7, 8, 11, and 15-17 is higher than the potential of iron in the corresponding mixtures 13, 14, 17, and 21-23.

Comparison of the rate of corrosion with the ultimate cathode current density shows that the rate of corrosion of iron in the passive state is lower than the ultimate cathode current density (Mixtures 1-5, 9, and 10). The rate of active corrosion is higher than the ultimate cathode current density (Mixtures 13, 14, and 18-30). In the instances of weakened active corrosion, the rate of corrosion is intermediate between the values of the ultimate cathode current densities measured with increasing current and those measured with diminishing current, or close to one of them (Mixtures 11, and 15-17).

Comparison of the ultimate cathode current density with the ultimate anode current density in relation to the corrosion activity of the reaction mixture yields the following results.

According to our measurements of the anodic polarization of the iron wire, the mixtures that passivate iron (Nos. 1-5, 9, and 10) yield ultimate anode current densities that are very small in comparison to the ultimate cathode current densities measured with increasing as well as with decreasing current values in the circuit. In actively corroding mixtures (Nos. 13, 14, and 18-30), the ultimate anode current densities greatly exceed the ultimate cathode current densities. Mixtures that exhibit an intermediate corrosion activity (Nos. 7, 11, and 15-17) yield ultimate anode current densities that are either close to (somewhat in excess of) the ultimate cathode current densities measured with increasing current or are the mean of the ultimate cathode current densities measured with increasing and with decreasing current values.

According to our measurements of the anodic polarization of the sheared-off iron wire, the mixtures that passivate iron exhibit an ultimate anode current density that is considerably lower than, or, in rare instances, close to, the ultimate cathode current density. Mixtures in which active or weakened active corrosion occurs exhibit

Table 1. Composition and Characteristics of the State of Reaction Mixtures

Mixture No.	Mixture composition, mols/liter		Mixture composition, molar percent			% of homopolar NO_2OH molecules.	Conc. of homopolar nitric acid mols/liter	% NO_2OH in vapor at 760 mm total pressure	B.p. at 760 mm. °C	Vapor pressure of nitric acid at 120°C, mm	Heat of formation from the constituents, Cal/100 mols.
	HNO_3	H_2SO_4	HNO_3	H_2SO_4	H_2O						
1	12.9	0	29.5	0	70.5	74	9.6	46	120	350	150
2	10.3	3.6	20.1	9.1	64.8	90	9.3	70	122	550	220
3	7.7	7.2	22.0	20.5	57.5	95	7.35	96	120	720	290
4	5.2	10.8	16.8	35.2	48.0	98	5.05	Beyond the measurement range	117	760	300
5	2.6	14.4	9.8	54.6	35.6	100	2.5		150	380	280
6	0	18.0	0	82.0	18.0	-	0	0	170	0	155
7	10.8	0	22.4	0	77.6	83	8.8	83	111.7	320	145
8	8.3	2.9	19.4	6.7	73.9	77	6.35	60	122	340	205
9	6.2	5.8	15.8	14.7	69.5	89	5.52	77	125	490	270
10	4.1	8.6	11.5	24.2	64.3	93	3.84	92	132	450	320?
11	2.1	11.5	6.4	35.8	57 8	97	2.0	93	155	270	350?
12	0	14.4	0	50 2	49.8	-	0	0	175	0	320?
13	7.7	0	16.0	0	84.0	47	3.6	12	112.5	140	120
14	6,2	2.2	13.5	4.7	81.8	60	3.7	23	117.5	200	170
15	4.6	4.3	10.8	10.0	79.2	72	3.65	33	123	200	215
16	3.1	6.5	7.6	16.0	76.4	80	2.5	47	131	260	265
17	1.54	8.6	4.1	22.8	73.1	88	1.85	64	148	140	285
18	0	10.8	0	30.6	69.4	-	0	0	172	0	310
19	5.2	0	10.1	0	90.0	25	1.30	0-1	107.5	10	95
20	4.1	1.4	8.4	2.9	88.6	32	1.30	1-2	110	24	105
21	3.1	2.9	6.5	6.1	87.4	42	1.30	3-5	112.5	52	150
22	2.1	4.3	4.5	9.4	86.8	48	1.00	5-7	117.5	53	190
23	1.04	5.8	2.4	13.1	84.5	58	0.60	8	121	58	205
24	0	7.2	0	17.0	83.0	-	0	0	-	0	250
25	2.6	0	4.8	0	95.0	≈0	≈0	≈0	-	≈0	50
26	2.1	0.7	3.9	1.4	94.5			≈0	-	≈0	65
27	1.54	1.4	3.0	2.8	94.2			≈0	-	≈0	75
28	1.04	2.2	2.1	4.3	93.7			≈0	-	≈0	100
29	0.52	2.9	1.0	5.8	93.2			≈0	-	≈0	125
30	0	3.6	0	7.4	92.7			0		0	145

Table 2

Rate of Corrosion and Potential of Corroding Iron. Ultimate Cathode and Anode Current Densities

Mixture No.	C (in gFe/cm²·hr)	C (in ma/cm²)	E_{Fe} (in mv)	I_{cb} (in ma/cm²)	I_{ca} (in ma/cm²)	I'_{cb} (in ma/cm²)	I'_{ca} (in ma/cm²)	Electrode: sheared-off wire		Electrode: wire 1 cm long		
								I_{ab} (in ma/cm²)	I_{aa} (in ma/cm²)	I_{ab} (in ma/cm²)	I_{aa} (in ma/cm²)	$I_{a_{max}}$ (in ma/cm²)
1	0.035	33.8	+670	10000	8430	8440	10000	∞	∞	470	376	>6250
2	0.038	36.2	+680				-	5500	750	31.3	25	>6250
	12.0	11600	-250	>7500								
3	0.020	19.4	+600	>5200				500	500	≈0	≈0	438
4	0.0007	0.63	+620	340	375	363	313	100	100	≈0	≈0	81
5	0.0003	0.25	+670	480	660	657	481	50	50	≈0	≈0	25
6	0.0012	1.25	-360	0	0	0	0	≈0	≈0	31.3	6.25	31.3
7	1.11	1070	- 25	950	750	81	113	∞	∞	1560	1250	>6250
8	0.80	770	-110	5200	4120	875	1000	15000	1500	362	300	>6200
9	0.011	10.6	+660	6180	5000	2260	2560	3000	2260	156	125	6200
10	0.06	57.5	≈+300	560	407	94	125	250	400	0	0	5000
11	0.018	16.3	-200	12.5	10.6	3.1	3.7	100	100	15.6	11.2	94
12	0.00084	0.81	-407	0	0	0	0	250	0	37.6	6.25	37.6
13	1.60	1540	- 85	14.4	11.9	4.4	5.6	∞	∞	3760	2940	>6250
14	0.722	695	-222	100	75	56	81	50000	500	1560	1690	>6250
15	0.270	260	-230	812	593	188	282	10000	1500	940	750	>6250
16	0.255	238	-185	1500	1000	81	106	3500	450	344	280	5620
17	0.128	125	-249	263	200	6.3	12.5	1750	1350	94	75	940
18	0.00083	0.88	-435	0		0	0	1250	1250	23.2	17.0	
19	1.17	1130	-224	1.3	3.1	<1.3	0	∞	∞			
20	0.433	420	-300	4.0	3.8	<1.3	0	∞	∞	>2000		
21	0.338	326	-303	3.1	5.0	≈0	0	∞	∞	1850	1400	
22	0.243	231	-326	6.3	9.4	3.1	3.1	10000	950	1800	1380	
23	0.145	138	-338	3.1	5.0	1.3	≈0	6250	1500	1380	1060	
24	0.0012	1.13	-455	0	0	0	0	5000	4000	1000	750	
25	0.820	788	-239	≈0	≈0	≈0	≈0					
26	0.319	306	-320	≈0	≈0	≈0	≈0					
27	0.192	183	-333	≈0	≈0	≈0	≈0			>2000		
28	0.100	93.8	-352	≈0	≈0	≈0	≈0			1800	1380	
29	0.063	62.5	-362	≈0	≈0	≈0	≈0			1800	1380	
30	0.00093	0.90	-457	0	0	0	0			1800	1380	

an ultimate anode current density that considerably exceeds the ultimate cathode current density (Mixtures 7, 8, 13-15, and 18-30).

The ultimate cathode and anode current densities and the corrosion activity are directly related to the state of the reaction mixtures, given in Table 1.

When the percentage of homopolar molecules of nitric acid are the same (Mixtures 1, 8, 15-16; 7, 14, 23; 4, 11) or when they all vary in the same direction (Mixtures 1, 7, 13, 19; 8, 14, 20; 9, 15, 21), the variation of the ultimate cathode current density parallels the change in the concentration of homopolar molecules of nitric acid. At concentrations of the homopolar nitric acid molecules that do not differ much (Mixtures 7, 8, 9; 13, 14, 15; 19, 20, 21), the variation of the ultimate cathode current density parallels the change in their degree of dissociation. We can also trace the parallelism between the ultimate cathode current density and the nitric acid vapor pressure (mixture groups 1 5, 7 11, 13 17). When the concentration and the vapor pressure of homopolar nitric acid both approach 0, no ultimate cathode current density is observed.

All these data indicate that the ultimate cathode current density is directly related to the concentration and the activity of the homopolar molecules of the nitric acid, and that it is these molecules that are the cathode depolarizers of the high-potential cathode process.

The ultimate anode current density diminishes when the relative and absolute amounts of sulfuric acid in the mixtures increase simultaneously with a decrease in the total percentage of water (the mixture groups 1-6; 7-12; 13-18, and 19-24). When the concentration of nitric acid equals the concentration of sulfuric acid (mixtures 1, 7, 13, 19; 2, 8, 14, 20; 3, 9, 15, 21, etc.) the less water in the mixtures and the higher the aggregate acid concentration, the lower is the ultimate anode current density. At identical molar percentages of water (Mixtures 1, 9, 18; 2, 10; 3, 11; 7,8, 16; and 13, 23) the ultimate anode current density diminishes as the percentage of sulfuric acid rises. In all the foregoing instances, the drop in the ultimate anode current density is accompanied by an increase in the percentage of homopolar molecules of nitric acid (degree of association), in the percentage of nitric acid in the vapor above the mixture, and in the heat of formation of the mixture from its components.

It is apparent that the degree of association of the molecules of nitric acid and the degree of association of the molecules of sulfuric acid vary in the same way in ternary systems. The percentage of nitric acid in the vapor above the mixture expresses the relative activity of the homopolar nitric acid and water in it. The heat of formation of the mixture from its components is directly related to the amount of water used to hydrate the acids. It follows that the lower the percentage and the activity of the molecules of water in the mixture, the lower the percentage of free NO_3' and SO_4'' ions, and the higher the percentage and the activity of the homopolar molecules of nitric acid, the more easily will anodic passivation occur. In binary H_2SO_4 - H_2O mixtures (Nos. 6, 12, 18, 24, and 30) and in ternary systems with a relatively high percentage of sulfuric acid (Mixtures 5, 11, 17, 23, and 29), anodic passivation at low current densities takes place at total acid concentrations in excess of 10 to 11 mols per liter (27-31 molar %). These are the concentrations at which the molecules of sulfuric acid dissociate chiefly into HSO_4' ions.

Instances of natural passivation of iron (Mixtures 1-5, 9, and 10) are featured by a high concentration of homopolar nitric acid molecules, a high degree of association and a high vapor pressure of the nitric acid, and a high heat of formation of the mixture from its components. Thus, the state of mixtures that passivate iron in its natural dissolution coincides with the state of mixtures in which anodic passivation takes place most readily.

An anode that is passivated in mixtures containing a high relative percentage of nitric acid retains a high electrical conductivity. In these media the maximum current density (for zero external resistance) is extremely high or greatly exceeds the ultimate anode current density. In mixtures containing a high percentage of sulfuric acid (Nos. 4, 5, 6, 11, and 12), the passivated anode loses its electrical conductivity. In these mixtures the anode current density is close to the ultimate anode current density and is small.

Evaluation of results. On the basis of our experimental data and some theoretical considerations we may set down the following hypothesis concerning the probable mechanism of the process of anodic passivation of iron in mixtures of nitric acid, sulfuric acid, and water.

In mixtures containing relatively few NO_3' and SO_4'' ions, these ions may vanish completely at the surface of the anode after a certain current density has been reached. In mixtures containing little or no sulfuric acid, however, either water molecules or associated complexes of hydrated H^+ and NO_3' ions, or, lastly, homopolar nitric acid molecules will react with the anode. It may be assumed that these molecules are first adsorbed at the anode by means of their oxygen molecules, then – in a highly polarized state – break down and yield up their positively-charged portions to the solution and leave the oxygen ions adsorbed to the anode. At potentials that are able to reduce homopolar molecules of nitric acid and at the same time are high enough for the irreversible passivating adsorption of oxygen ions, the detachment of these latter from the nitric acid molecules is facilitated and may occur together with their reduction. It is possible that different particles will prove to be passivated at different, sufficiently high, potentials. When this is so, the passivation of particles to which the oxygen ions are attached most firmly may cause the anode potential to reach a value at which other particles will lose electrons and under this sort of decomposition release oxygen. The passivated anode will possess a definite conductivity, and this is actually found to be the case.

In mixtures containing relatively many NO_3' or SO_4'' ions, these ions are hydrated [8], with hydrogen ions abutting on them, while the oxygen ion is at some distance. The attraction of electrons from the oxygen ions of the hydrating water is weakened by the polarization due to the NO_3' and SO_4'' ions. The electron attraction is weak even in the oxygen atoms entering into the NO_3' and SO_4'' ions, since they possess an excess of negative charges. This is why, when a sufficiently high positive anode potential acts upon these anions or upon the oxygen ion of the hydrating molecule of water, it may prove to be easier to deliver electrons to the anode than to liberate an oxygen ion. When the electrons jump over to the anode, an oxygen atom is formed, not from a liberated oxygen ion that is drawn to the anode, but as the result of the decomposition of the remaining complexes that follows the delivery of the electrons. In this case the evolution of free oxygen is more likely than the adsorption of an oxygen ion by the anode, which could result in the latter's passivation. Hence, the presence of large numbers of NO_3' or SO_4'' ions or both ought to interfere with the passivation of the anode. In actuality, the ultimate anode current density increases greatly as the percentage of NO_3' and SO_4'' ions is increased during the dilution of concentrated mixtures. The appearance of SO_4'' ions when small quantities of sulfuric acid are added to a passivating solution of nitric acid (Mixture 2) may explain the development of extremely high activity of the corrosion process.

In mixtures that contain a preponderant percentage of nitric acid, in which there are still fewer NO_3' ions and enough HSO_4' ions, the reaction of the latter ions with the anode ought to be the principal factor. Of these ions it must be said that it ought to be harder to detach electrons or oxygen ions from them owing to their struc-

structure and the relatively small excess of negative charge. There is an indication that the discharge potential of the HSO_4' ion is higher than the normal oxygen discharge potential [35a]. The very HSO_4' ions adsorbed at the anode may constitute an electrochemical shield that passivates it. Moreover, these ions, polarized by the anode in such a fashion that their ends that face the liquid acquire a positive pole that is not discharged, may cover the anode in several layers. This is how the loss in conductivity may come about. To confirm the assumption that passivation is due to the HSO_4' ions in mixtures containing a high percentage of sulfuric acid, we measured the ultimate anode current density at a platinum electrode – a wire cut off at the glass – in the non-passivating Mixture 30, consisting of sulfuric acid and water, to which Mohr's salt, ammonium sulfate, and sodium bisulfate had been added to saturation. No ultimate anode current density was found in the first two cases. On the other hand, when 19 milliamps was reached in Mixture 30, saturated with $NaHSO_4$, the current jumped 0.6 milliamp. The latter value did not change when the external resistance was reduced to zero. Mixture 29, saturated with the same salt, exhibited an ultimate anode current of 22 → 0.3 milliamp. Its iron corrosion was found to be 0.0036 g Fe per cm^2 per hour.

In mixtures containing a high percentage of sulfuric acid, passivation may also be explained as the result of the adsorption of acid ions of persulfuric acid, HS_2O_8' which are formed during the anodic oxidation of sulfuric acid. It may well be that in various media passivation is effected by the adsorption of either HSO_4' ions or of HS_2O_8' ions. The latter, possessing a much stronger internal positive field, must retain their excess electron with great force; that is why HS_2O_8' ions replace HSO_4' ions under conditions when the latter would lose their charge. The conditions at which passivation takes place in mixtures containing a relatively large percentage of sulfuric acid fully correspond to the conditions for the formation of persulfuric acid and persulfates during the anodic oxidation of sulfuric acid and sulfates. Thus, persulfuric acid is not formed at low concentrations of sulfuric acid, at which the iron anode is not passivated, though it is formed within a wide range of acid concentrations and current densities at medium and high sulfuric-acid concentrations. Raising the anode potential and the sulfuric-acid concentration facilitates the formation of persulfates and a passive state of the iron. An electrolyte containing Na_4HSO_4 is recommended for producing a persulfate; after our non-passivating Mixtures 29 and 30 had been saturated with $NaHSO_4$, the ultimate anode current density that could not be measured before made its appearance, and the iron undergoing natural corrosion began to be passivated in Mixture 29. As the concentration of sulfuric acid is raised, the solubility of the persulfates and the ultimate anode current density drop, according to our measurements. Nitric acid prevents the formation of persulfates, and the ultimate current density is extremely high in our mixtures containing a high percentage of this acid, [35b].

The disclosed relationship of corrosion activity, ultimate cathode current density, and ultimate anode current density, the relationship of all of them to the state of the reaction media, and the proposed hypothesis on the mechanism of anodic passivation enables one to reach a certain probable conclusion of the mechanism of the passivation of self-dissolving iron as well.

The passivation of iron in the system under study may be conceived of as taking place as follows:

Nitric acid in the form of homopolar molecules is a reagent that interacts directly with the electrons of the metal phase to give the latter a high-potential state. Besides our own data, this assertion is in full conformity with the much sharper rise in the potential of iron in solutions of nitric acid, which is accompanied by the appearance and increase in the concentration of homopolar nitric acid molecules in them. The iron potential rises evenly and relatively slowly, beginning

with a 0.001 N solution of nitric acid, in which it has a rather high negative value, to a 3 N solution. In the concentration range of 3 N to 10 N the potential rises sharply to values that are typical of the passive state [17]. According to the data of Table 1, the concentration of homopolar molecules rises from 0 to 6.4 N during a transition from a 2.6 N to a 10.3 N solution of nitric acid. The concentration of nitric acid below which all the acid exists in the form of ions and above which homopolar molecules begin to appear is 3.15 N [7].

It should be said that though there is a quite close and direct link between passivation and the concentration and activity of homopolar nitric acid molecules, there is no need to consider nitrogen dioxide to be the passivating agent in solutions of nitric acid, as Evans does [19].

In media in which the ultimate anode current density over the entire anode surface is lower than the ultimate cathode current density over all the cathode surface and lies in the range of rather high potentials of the cathode polarization curve, all the conditions are present that are required for passivating the anode surface. The cathode process that takes place during the natural interaction of the metal with the reaction medium is able to make the anode current reach such values and to raise the anode surface to a potential at which it must reach a passive state. The iron must be passivated in such media.

This conception of the general mechanism of the passivation process, which is the direct outcome of experimental data, agrees on the whole with the concept described in the paper by Tomasov, Sinelshchikova, and Vedeneyeva [38].

The nature of passivation of the anode surface of a self-dissolving metal in mixtures in which nitric acid predominates differs from that in mixtures where the sulfuric acid predominates. In the former it is the result of adsorption or of the formation of a surface compound of the metal with oxygen ions detached from the homopolar molecules of nitric acid, the associated complexes of hydrated H^+ and NO_3^- ions, or the molecules of water. The latter two cases will be more likely, when the medium contains a cathode depolarizer that produces a potential sufficiently positive to detach oxygen ions. Homopolar molecules of nitric acid may be such a depolarizer with respect to the water molecules and the associated complexes of hydrated H^+ and NO_3^- ions. The assertion made in one of the references in the literature [28c] that iron is not passivated in highly concentrated nitric acid, containing more than 94% HNO_3, because of the insufficiency of water, may be explained theoretically on the basis of the passivation mechanism proposed by us. Since there is no free water in such acids, there are no molecules from which oxygen ions could be detached to passivate the iron under the action of the cathode depolarizing forces of the homopolar nitric acid molecules.

The participation of water molecules in the anodic process and in the passivation of a metal in solutions of strong oxidants is probable from the thermodynamic standpoint and is in agreement with the decomposition of water and the ensuing liberation of oxygen that occurs in these processes [37].

The HSO_4^- and $HS_2O_8^-$ ions are adsorbed or are given a definite orientation in mixtures containing a preponderance of sulfuric acid when the anode surface is at a high potential, which also produces cathodic depolarization of the homopolar molecules of nitric acid. Thus, the resulting adsorption layer, which probably consists of more than one layer of anions, possesses very low conductivity.

SUMMARY

1. The rate of corrosion of iron, its potential during corrosion, the ultimate cathode current density at a smooth platinum electrode, and the ultimate anode current density at an iron electrode have been determined in mixtures of nitric acid, sulfuric

acid, and water. Data in the literature have been drawn on to describe the state of the reaction mixtures.

2. Experimental data show that self-dissolving iron is passivated when the maximum rate of the high-potential cathodic process in an oxidizing reaction medium (the ultimate cathode current density) exceeds the maximum rate of the low potential, active, anodic process (ultimate anode current density).

3. The probable mechanism of the anodic passivation of iron in mixtures containing a relatively high percentage of nitric acid (which is in accordance with the experimental data) consists of the anodic adsorption of molecules of water, associated complexes consisting of hydrated H^+ and NO_3^- ions, or homopolar molecules of NO_2OH, followed by the detaching of oxygen ions from them and the formation of a surface compound. In mixtures containing a preponderance of sulfuric acid, passivation is due to the anodic adsorption of HSO_4^- or $HS_2O_8^-$ ions.

4. The correspondence of these passivation conditions indicates that the nature of the anodic process that takes place during the passivation of self-dissolving iron is the same as that occurring during anodic passivation. The passivation of self-dissolving iron results from an anodic process, whose rate exceeds the ultimate anode current density in the given medium. The high velocity of the anodic process during the natural dissolution of the metal entails a high velocity of the high-potential cathodic process, which consists of the reaction of the homopolar molecules of nitric acid with the electrons of the metal phase.

LITERATURE CITED

[1] A.Sapozhnikov. J. Russ. Phys. Chem. Soc. 41, 1712 (1909).

[2] A.Hantzsch Ber., 15, 941 (1925).

[3] A.Hantzsch u. K. Berger, Ber., 61, 1328 (1928).

[4] H.V.Halban u. Eisenbrand, Z. physik. Chem., 131, 433 (1928).

[5] O.Redrich, Z. physik. Chem., A, 182, 42 (1938).

[6] M.R.Dalmon, Compte rend., 207, 473 (1938).

[7] J.Chedin, Ann. chim., 8, 243 (1937); Memorial des poudres, 28, 7 (1938).

[8] A.I.Kazmin, J. Phys. Chem. USSR, 11, 585 (1938).

[9] P.S.Spasokukotsky, Prog. Chem., 17, 55 (1948).

[10] M.Sh. Gelfman, J. Appl. Chem., 21, 1099 (1948).

[11] M.Sh. Gelfman, J.Appl. Chem., 21, 1272 (1948).

[12] I.I.Zaslavsky, J.Gen.Chem. 19, 995 (1949).*

[13] O.M.Klimova and I.I.Zaslavsky, J. Appl. Chem. 22, 689 (1949).

[14] A.N.Krestovnikov and I.Ya.Klinov, J.Chem. Ind., USSR, 8, 14 (1945).

[15] A.M.Ivanova, Corrosion and Its Prevention (USSR), 7, 1, 53 (1941).

[16] M.S.Golombik, M.M.Levina, and N.N.Petin, J. Phys. Chem. USSR, 13, 425 (1939).

[17] G.V.Akimov and V.P.Batrakov, Proc. Acad. Sci. USSR (Doklady), 45, 124 (1944).

[18] G.V.Akimov. The Theory and Research Methods of Metal Corrosion, 201 (1945).

[19] U.R.Evans. Corrosion, Passivity, and Metal Protection, 32, 33, 62-68 (1945).

*Cf. CB translation p 985 ff

[20] V.Cupr, Korrosion u. Metallschutz, 19, 130 (1943).

[21] E.Pietsch. Korrosion u. Metallschutz, 8, 57 (1932).

[22] B.V. Ershler, Proc. (Doklady) USSR Acad. Sci., 37, 258, 262 (1942).

[23] B.V.Ershler, J. Phys. Chem. USSR, 18, 131 (1944).

[24] A.N.Frumkin, Prog. Chem. 15, 585 (1946).

[25] W.J.Schutt, A.Walton, Trans. Faraday Soc., 28, 740 (1932).

[26] L.K.Lepin, Prog. Chem., 7, 4 (1938).

[27] K.F.Bonhoeffer, Z. Elektrochem., 47, 147 (1941).

[28] Y.Yamamoto, Bull. Inst. Phys. Chem. Research (Tokyo), (Abstracts): a) 15, 12, 69 (1936); b) 15, 9, 52 (1936); c) 18, 2, 7 (1939).

[29] U.R.Evans, Trans. Faraday. Soc., 40, 120 (1944).

[30] E.S.Hades, J. Chem. Soc., a) 968 (1928); b) 2878 (1926).

[31] W.D.Bancroft and J.D.Porter, J. Phys. Chem. London, 40, 37 (1936).

[32] M.S.Golombik, N.N.Petin, and O.P. Yukhnovskaya, J. Phys. Chem USSR, 17, 740 (1940).

[33] Technical Encylcopedia: Hdbk. Phys.Chem. and Eng. Data., Vol. 3, 471 (1950).

[34] Kondratsky, Trans. Kazan Inst. Chem. Technol. 7, 145 (1938).

[35]S. Glasstone and A.Hickling. Electrolytic Oxidation and Redution: a) 267; b) 258-267 (1935).

[36] N.D.Tomashov, G.P.Sinelshchikova, and M.A.Vedenyeeva, J.Phys. Chem., 23, 289 (1949).

[37] A.N.Shultin, J. Appl. Chem. 20, 739 (1947).

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THE DECOMPOSITION VOLTAGE (EQUILIBRIUM REACTION POTENTIAL) OF ALKALOID SALTS AND THE FORMATION VOLTAGE OF ALKALOIDS FROM THEIR SALTS*

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A study of the literature [1-7] on the recovery of alkaloids by electrolysis led us to the following conclusions:

1) Very little attention has been paid up to the present time to the problem of the recovery of alkaloids by means of electrolysis.

2) The few papers published in this field are chiefly experimental ones.

3) In addition to research of an empirical nature, devoted to the isolation of individual alkaloids or the development of methods for such isolation, closer theoretical and experimental research is required on the underlying factors affecting this process.

4) The development of merely empirical methods of electrolytically recovering alkaloids, without parallel theoretical study, may yield false results. Oficjalski [7], for instance, concluded that the bases of these alkaloids must not be isolated during the electrodialysis of salts of morphine, cocaine, and atropine, since the alkaloids undergo oxidation during the process of electrodialysis, and by-products are formed. It must be pointed out, however, that Oficjalski used a voltage of 120 volts to isolate the alkaloids from their salts. We have shown that once one possesses data on the decomposition voltages of morphine, cocaine, and atropine salts, these alkaloids can be recovered without suffering any change.

We felt that not only would a study of the decomposition voltages of salts of the alkaloids be of theoretical interest, but that the decomposition-voltage values could point to the electrolysis procedure required to isolate the alkaloids.

As we know, the decomposition voltage is the minimum voltage applied to the electrodes at which the process of electrolysis sets in. We assumed that the decomposition voltages of the alkaloid salts must be clearly marked, inasmuch as crystalline deposits and the evolution of gas (hydrogen) are observed at the cathode in most cases when current is passed through solutions of alkaloid salts:

$$(RH\cdot H)X \rightleftarrows (RH\cdot H)^+ + X^-$$

$$(RH\cdot H)^+ + e = \underset{\text{(deposit)}}{RH} + \tfrac{y}{2}H_2$$

RH = alkaloid base; X = acid anion.

We expected aqueous solutions of the alkaloid salts to exhibit higher values of the decomposition voltage than aqueous solutions of inorganic bases and acids or their salts, since alkaloid salts, which are organic compounds, tend to increase the hydrogen overvoltage.

In our research we found that the hydrogen overvoltage is also of great practical importance, and we therefore made a study of the decomposition voltage of aqueous solutions of alkaloid salts at platinum electrodes as well as at electrodes made of other materials.

EXPERIMENTAL

The following alkaloid salts were used in our research:

1) The hydrochlorides of morphine, methylmorphine, ethylmorphine, diacetylmorphine, cocaine, quinine, emetine, salsoline, ephedrine, lobeline, papaverine, and pilocarpine; 2) strychnine nitrate; 3) atropine sulfate; and 4) physostigmine salicylate.

0.025 N aqueous solutions of these salts were prepared. We used this concentration because of the low solubility of some alkaloid salts. For example, 1 part of strychnine nitrate dissolves in 90 parts of water at 20°; 1 part of physostigmine dissolves in 100 parts of water; 1 part of papaverine hydrochloride dissolves in 40 parts of water; 1 part of quinine hydrochloride in 30 parts of water; and 1 part of morphine hydrochloride dissolves in 25 parts of water.

Method of measuring the decomposition voltage. The method of "current variation with voltage" was used for these measurements.

Voltage was applied to the cell by means of a rheostat, connected to a storage-battery circuit through a potentiometer. A voltmeter and a mirror galvanometer were connected in the circuit to read the voltage and current.

The following metals were used as electrodes: platinum, mercury, silver, copper, lead, nickel, cadmium, iron, zinc, aluminum, and ER-1 steel, as well as carbon. The electrodes had the shape of needles or thin platelets. The areas of the immersed portions of the cathode and anode totaled 10 mm^2. The distance between the electrodes was 15 mm. The voltage was raised in 0.1 volt steps by adjusting the potentiometer, waiting each time until the current reached a constant value (this was done by observing the galvanometer); this took three to five minutes. At least 10 determinations were made for each solution at the given concentration, the mean value being taken. All determinations were made at 20°C.

We determined the decomposition voltage from the points where the curves bent. The appearance of bubbles of gas at the electrodes during the process of measurement was taken as the start of electrolysis. We also read the e.m.f. at which the separation of crystals from the alkaloid salt solutions was observed to occur. The e.m.f. at which crystals were observed to separate out of the alkaloid salt solution was called the alkaloid separation voltage.

Our results are shown in Figs. 1-2 and in Tables 1-4.

The crystals deposited on and at the cathode were collected on a filter and

TABLE 1

Decomposition Voltages of a 0.025 N Solution of Strychnine Nitrate and the Strychnine Separation Voltage

Electrode material		Decomposition voltage, obtained graphically	Voltage at which strychnine begins to be formed, volts	Electrode material		Decomposition voltage, obtained graphically	Voltage at which strychnine begins to be formed, volts
Anode	Cathode			Anode	Cathode		
Platinum	Platinum	2.5	2.5	Steel	Platinum	2.1	2.3
"	Aluminum	-	2.9	Aluminum	"	-	0.3
"	Zinc	-	2.2	Zinc	"	-	0.4
"	Iron	-	2.0	Iron	"	-	0.4
"	Cadmium	-	2.7	Cadmium	"	-	0.6
"	Nickel	-	2.6	Nickel	"	-	1.9
"	Lead	-	2.8	Lead	"	-	0.7
"	Copper	2.6	2.6	Copper	"	-	1.0
"	Silver	-	2.5	Silver	"	-	0.9
"	Mercury	2.7	2.7	Mercury	"	1.0	1.0
"	Steel	2.25	2.6	Aluminum	Steel	0.25	0.4
Steel	Steel	2.0	2.2	Zinc	"	-	0.5
"	Aluminum	-	2.8	Iron	"	-	0.5
"	Zinc	-	2.6	Cadmium	"	-	0.6
"	Iron	-	2.4	Nickel	"	-	2.0
"	Cadmium	-	2.5	Lead	"	-	0.6
"	Nickel	-	2.6	Copper	"	-	1.1
"	Lead	-	2.6	Silver	"	-	1.0
"	Copper	-	2.6	Mercury	"	0.75	1.2
"	Silver	-	2.6	Carbon	Carbon	-	2.1
"	Mercury	2.5	2.6				

washed with water until all the alkaloid salt had been eliminated. The washed crystals were desiccated for two hours in a drying chamber, after which they were carefully pulverized in a mortar and placed in a capillary. The capillary was attached to a thermometer, and the melting point was determined.

The melting points of the crystals recovered from the hydrochlorides of morphine, diacetylmorphine narcotine, cocaine, quinine, emetine, and lobeline, and from the nitrates of strychnine and brucine are listed in Table 5.

The crystals recovered from the alkaloid salts were also tested for their solubility in organic solvents. Specific reactions were performed to test the genuineness of each alkaloid.

All the crystals recovered were readily soluble in chloroform, ether, or methanol (morphine).

The special reactions for each alkaloid were positive. Thus, the crystals recovered from morphine hydrochloride produced a purple color, changing to blue, with Frede's reagent after having been washed with water and dissolved in 1 to 2 drops of dilute hydrochloric acid; the crystals recovered from strychnine nitrate and treated as set forth above formed blue-purple streaks, changing to red and dirty-green, when

TABLE 2

Decomposition Voltages of a 0.025 N Solution of Morphine Hydrochloride and the Morphine Formation Voltage

Electrode material		Decomposition voltage, obtained graphically	Voltage at which strychnine begins to be formed, volts	Electrode material		Decomposition voltage, obtained graphically	Voltage at which strychnine begins to be formed, volts
Anode	Cathode			Anode	Cathode		
Platinum	Platinum	2.5	2.5	Steel	Aluminum	–	2.0
"	Aluminum	–	2.8	"	Zinc	–	1.5
"	Zinc	–	2.1	"	Iron	–	1.6
"	Iron	–	2.3	"	Cadmium	–	1.5
"	Cadmium	–	2.5	"	Nickel	–	1.6
"	Nickel	–	2.0	"	Lead	–	1.5
"	Lead	–	2.7	"	Copper	–	1.6
"	Copper	–	2.6	"	Silver	–	1.3
"	Silver	–	2.3	"	Mercury	1.7	1.8
"	Mercury	2.8	2.8	"	Platinum	1.0	1.3
"	Steel	2.2	2.3	Aluminum	"	0.25	0.5
Steel	"	1.25	1.4	Zinc	"	–	0.6
Iron	Platinum	–	0.8	Iron	Steel	–	0.5
Cadmium	"	–	0.8	Cadmium	"	–	0.6
Nickel	"	–	1.6	Nickel	"	–	1.4
Lead	"	–	0.9	Lead	"	–	0.7
Copper	"	–	0.9	Copper	"	–	1.0
Silver	"	–	0.9	Silver	"	–	0.9
Mercury	"	0.6	0.9	Mercury	"	0.9	1.0
Aluminum	Steel	0.2	0.4	Carbon	Carbon	–	2.1
Zinc	"	–	0.4				

reacted with concentrated sulfuric acid and a tiny crystal of potassium bichromate; the addition of a 1% solution of potassium permanganate to crystals of cocaine dissolved in 0.1 N hydrochloric acid produced a precipitate which had the appearance of rectangular and square pinkish-violet platelets when viewed under the microscope; the crystals of quinine exhibited light-blue fluorescence in sulfuric acid.

We performed experiments with various concentrations of aqueous solutions of morphine, cocaine, and strychnine salts to shed light on the problem of the effect of the concentration of solutions of the alkaloid salts upon the magnitude of the decomposition voltage. The results obtained are listed in Table 6.

The effect of the current density upon the size of the decomposition voltage was explored in 0.025 N aqueous solutions of morphine and cocaine hydrochlorides and strychnine nitrate. Our results are given in Table 7.

We investigated the decomposition of ammonium chloride as the simplest example of a salt of a nitrogenous base $(H_3N \cdot H)Cl$, in order to make a comparison of the decomposition voltage of the alkaloid salts with that of salts of inorganic bases.

Our results are shown in Table 8 and Figs. 3-4.

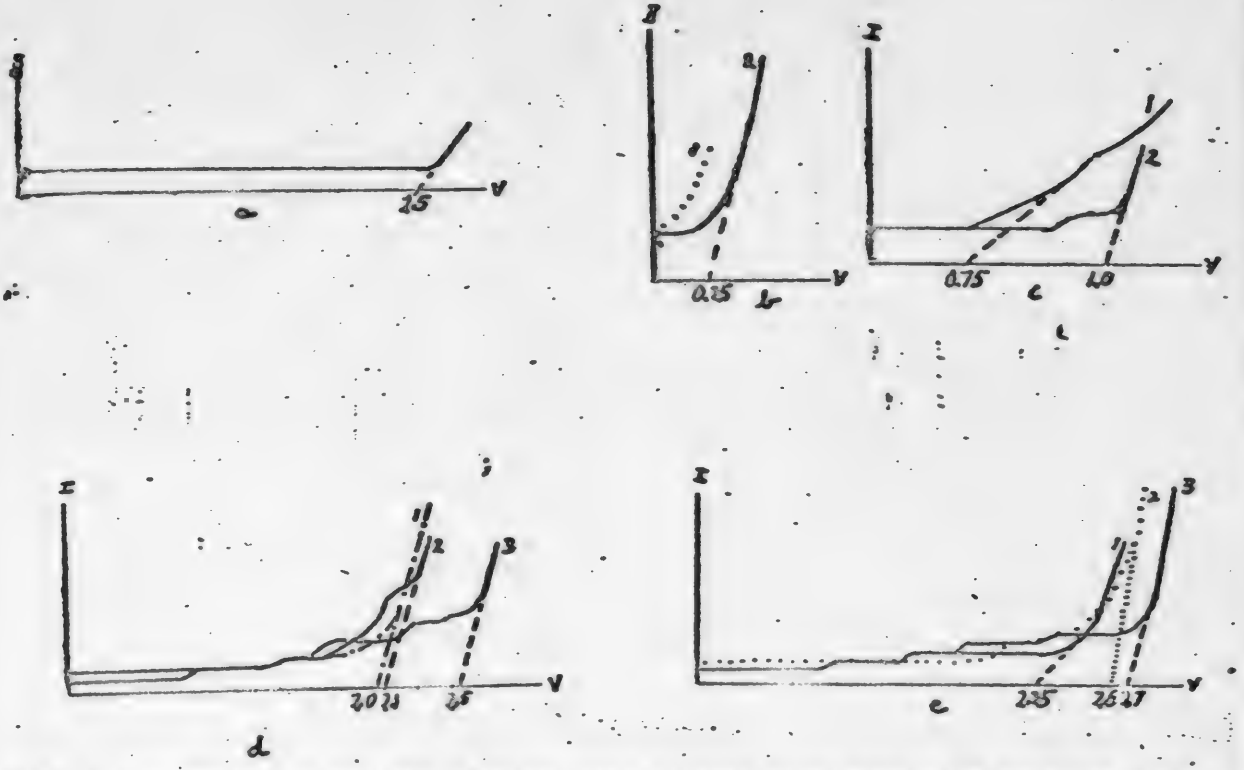

Fig. 1. Decomposition voltage of strychnine nitrate using various electrodes. Concentration: 0.025 N. 2 mm = 1 division on the galvanometer scale; 4 mm = 0.1 V.

a) Electrodes: Pt-Pt; b) electrodes: 1- Al-Pt; 2- Al-Steel; c) electrodes: 1- Hg-steel; 2- Hg-Pt; d) electrodes: 1- steel-steel; 2- steel-Pt; 3- steel-Hg; e) electrodes: 1- Pt-steel; 2- Pt-Cu; 2- Pt-Hg.

TABLE 3

Decomposition Voltages of 0.025 N Aqueous Solutions of Alkaloid Salts at Platinum and Steel Electrodes

Alkaloid Salt	Electrode		Alkaloid salt	Electrode	
	Platinum-Platinum	Steel-Steel		Platinum-Platinum	Steel-Steel
Cocaine hydrochloride	2.4	1.9	Quinine dihydrochloride	3.4	2.4
Methylmorphine hydrochloride	2.4	1.9	Pilocarpine hydrochloride	2.3	1.0
Ethylmorphine hydrochloride	2.4	1.1	Ephedrine hydrochloride	2.4	1.3
Diacetylmorphine hydrochloride	2.7	1.4	Salsoline hydrochloride	2.3	1.1
Papaverine hydrochloride	2.4	1.0	Lobeline hydrochloride	2.7	0.9
Emetine hydrochloride	2.8	1.3	Atropine sulfate	2.45	2.2
Quinine hydrochloride	5.5	3.5	Physostigmine salicylate	2.9	2.8

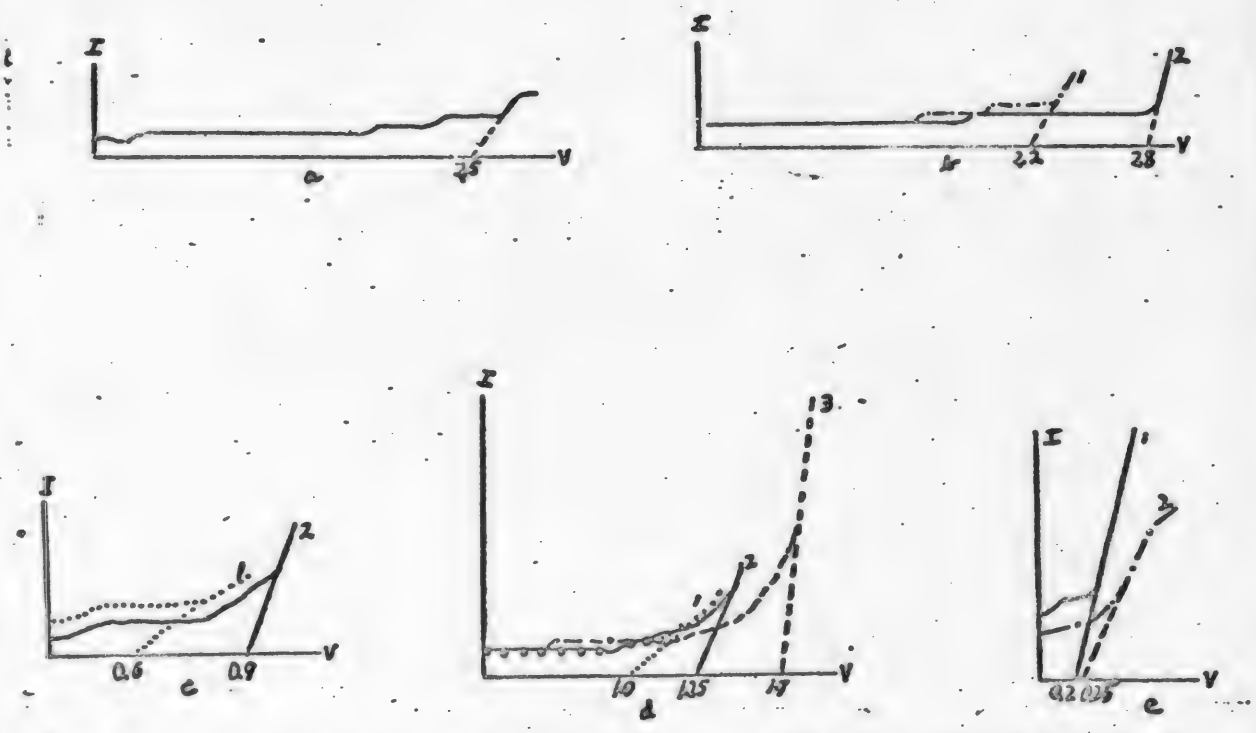

Fig. 2. Decomposition voltage of morphine hydrochloride using various electrodes. Concentration: 0.025 N.

a) electrodes: Pt-Pt; b) electrodes 1- Pt steel; 2- Pt Hg; c) electrodes: 1- Hg-Pt; 2- Hg-steel; d) electrodes: 1- steel-Pt; 2- steel-steel; 3- steel-Hg; e) electrodes: 1- Al-steel; 2- Al-Pt.

TABLE 4

Separation Voltages of Alkaloids from Aqueous Solutions (0.025 N) of Their Hydrochlorides

Alkaloid	Electrodes				Remarks
	Platinum* Platinum**	Steel* Steel**	Aluminum* Platinum**	Aluminum* Steel **	
Diacetylmorphine	2.8	1.6	0.5	0.6	
Papaverine	2.5	1.1	0.2	0.2	
Quinine	5.5	3.5	1.5	1.5	From quinine hydrochloride
Quinine	3.4	2.4	1.2	1.3	From quinine dihydrochloride
Emetine	3.0	1.5	0.6	0.8	
Ephedrine	-	1.5	0.3	0.6	
Salsoline	2.5	1.2	0.3	0.6	
Cocaine	2.4	2.0	0.7	0.7	

* anode ** cathode

TABLE 5

Melting Points of Crystals Recovered from Alkaloid Salts

Alkaloid salt		M.p. of the alkaloid base	
		In the literature	Our data
Hydrochlorides	morphine	Approx. 230°	228-230°
	diacetylmorphine	171°	169-171°
	narcotine	176	173-175°
	cocaine	98	97-98°
	quinine	174.6°	173-174°
	emetine	68° (no lower than)	69-70°
	lobeline	118-121°	118-119°
Nitrates	strychnine	265-266°	263-265°
	brucine	Above 100°	105-110°

TABLE 6

Decomposition Voltages of Various Concentrations of Aqueous Solutions of Alkaloid Salts at Platinum Electrodes

Alkaloid salt	Concentration	Decomposition voltage, volts
Morphine hydrochloride	0.025 N	2.50
	0.0125 N	2.45
	0.0062 N	2.50
	0.0031 N	2.50
	0.0015 N	2.75
Strychnine nitrate	0.025 N	2.50
	0.0125 N	2.40
	0.0062 N	2.45
	0.0031 N	2.45
	0.0015 N	2.60

Evaluation of results. In our determinations the decomposition voltage of a 1 N aqueous solution of ammonium chloride was found to be 1.74 volts at platinum electrodes (Fig. 3a).

This value is close to those obtained by Leblanc [8] and Murtazaev and Ablyaev [9].

Decomposition voltage of a 1 N solution of ammonium chloride in water at platinum electrodes (in volts)

Leblanc	Murtazaev and Ablyaev	Our data
1.70	1.76	1.74

The decomposition voltage of an aqueous solution of ammonia chloride depends upon the concentration, however. For example, the decomposition voltage at platinum electrodes is 1.74 volts for a 1 N solution, 2.25 volts for a 0.1 N solution, and 2.50 volts for a 0.025 N solution (Figs. 3b, 3c).

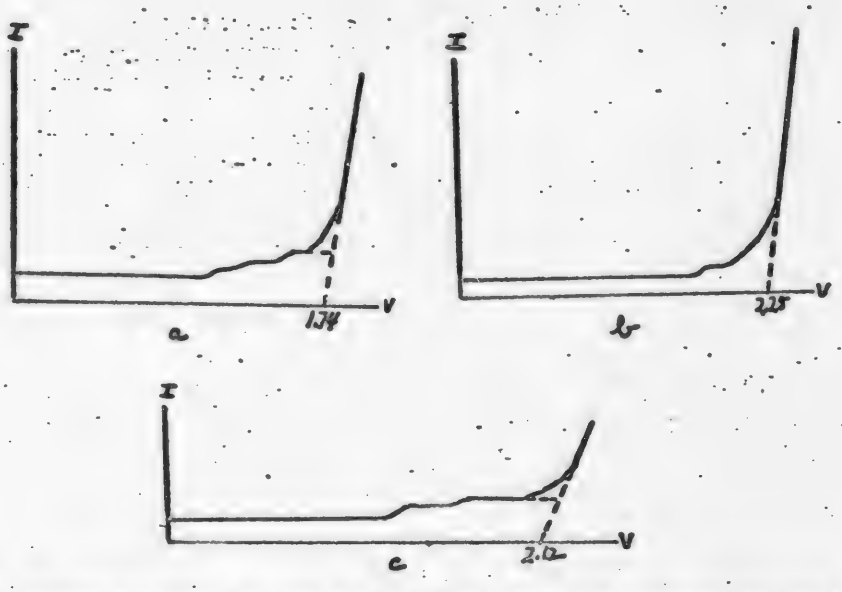

Fig. 3. Decomposition voltage of NH_4Cl at various concentrations. Electrodes: Pt - Pt. 2 mm = 0.1 volt; 4 mm = 1 division on the galvanometer scale.

a) NH_4Cl concentration - 1N; b) NH_4Cl concentration - 0.1N; c) NH_4Cl concentration - 0.025N.

TABLE 7

Decomposition Voltages of Alkaloid Salts at Platinum Electrodes as a Function of Current Density

Alkaloid salt	Concentration	Area of immersed portion		Decomposition voltage, volts
		Anode, mm^2	Cathode, mm^2	
Morphine hydrochloride	0.025 N	252	252	2.50
		252	126	2.25
		252	63	2.00
		252	21	2.35
		252	7	2.25
		252	5	2.35
Strychnine nitrate	0.025 N	252	252	2.50
		252	126	2.25
		252	63	2.00
		252	21	1.95
		252	7	1.90
		252	5	2.25

The results of our study of the decomposition voltage at electrodes of platinum (anode) and other metals (cathode), given in Table 8 and Fig. 4a, show that the decomposition voltage of a 0.1 N solution of ammonium chloride is highest at electrodes consisting of platinum (anode) and copper, mercury, or lead (cathode). These results are in conformity with the figures cited by various authors in connection with the

hydrogen overvoltage at the metals mentioned above. Measurments made in A.N. Frumkin's laboratory are cited for the sake of comparison (Fig. 5).

At electrodes consisting of platinum as the cathode with other metals as the anode, the decomposition of a 0.1 N aqueous solution of ammonium chloride is observed at voltages below 1 volt, the voltage rising from aluminum to mercury. Thus, bubbles are observed at a voltage of 0.1 volt with aluminum as the anode and platinum as the cathode, and at 0.7 volt with platinum as the cathode and mercury as the anode.

Hence, the decomposition of a solution of ammonium chloride sets in at increasing voltages if the anode metals are arranged in the order of their increasing negative standard potentials (voltage series).

In the experiments in which ER-1 steel was used as the anode and other metals served as the cathodes, the decomposition of the ammonium chloride solution set in at a lower voltage than when platinum was used as the anode with other metals serving as the cathodes. For example, the decomposition voltage of a 0.1 N solution of ammonium chloride is 2.25 volts at platinum electrodes (Fig. 3b), but only 1.5 volts at steel electrodes (Fig. 4b); the decomposition voltage is 3.45 volts when platinum is used as the anode and mercury as the cathode (Fig. 4a), and 2.3 volts when steel is used as the anode and mercury as the cathode (Fig. 4d).

When steel is used as the cathode with other metals as the anode, the decomposition of a 0.1 N ammonium chloride solution sets in at the same points as when platinum serves as the cathode and the other metals as the anode. Decomposition sets in at rising voltages when the anode metals are arranged according to their increasingly negative standard potentials.

Bearing in mind the fact that the decomposition voltage can be measured with satisfactory accuracy only when the electrodes are made of inert

TABLE 8

Decomposition voltages of a 0.1 N Solution of Ammonium Chloride at Electrodes of Different Materials

Electrode material		Decomposition Voltage (obtained graphically)	Voltage at which gas bubbles begin to evolve (V)
Anode	Cathode		
Platinum	Platinum	2.12	2.3
"	Aluminum	-	3.2
"	Zinc	-	2.4
"	Iron	-	2.2
"	Cadmium	-	2.4
"	Nickel	-	2.4
"	Lead	-	3.2
"	Copper	2.8	2.6
"	Silver	-	2.5
"	Mercury	3.3	3.0
"	Steel	2.5	2.4
Steel	Steel	1.5	1.5
"	Aluminum	-	1.5
"	Zinc	-	1.4
"	Iron	-	1.1
"	Cadmium	-	1.3
"	Nickel	-	1.4
"	Lead	-	1.6
"	Copper	1.6	1.6
"	Silver	-	1.6
"	Mercury	2.3	2.0
"	Platinum	1.5	1.2
Aluminum	Platinum	0.1	0.1
Zinc	"	-	0.2
Iron	"	-	0.3
Cadmium	"	-	0.5
Nickel	"	-	1.5
Lead	"	-	0.7
Copper	"	0.7	0.7
Silver	"	-	0.8
Mercury	"	0.7	0.7
Aluminum	Steel	0.4	0.2
Zinc	"	-	0.4
Iron	"	-	0.4
Cadmium	"	-	0.4
Nickel	"	-	1.3
Lead	"	-	0.6
Copper	"	-	0.9
Silver	"	-	0.8
Mercury	"	-	0.9
Carbon	Carbon	-	2.4

materials, we placed the anodes in a parchment capsule (thus separating the anode by a diaphragm) in the experiments in which soluble electrodes, such as aluminum, zinc, iron, etc., were employed.

The results obtained in the experiments in which a diaphragm was used coincided with those obtained in the experiments in which the decomposition of ammonium chloride was investigated at electrodes of various materials without any protective diaphragm.

The decomposition voltages of an aqueous solution of strychnine nitrate and the formation voltage of strychnine are given in Fig. 1 and Table 1. Our results indicate that:

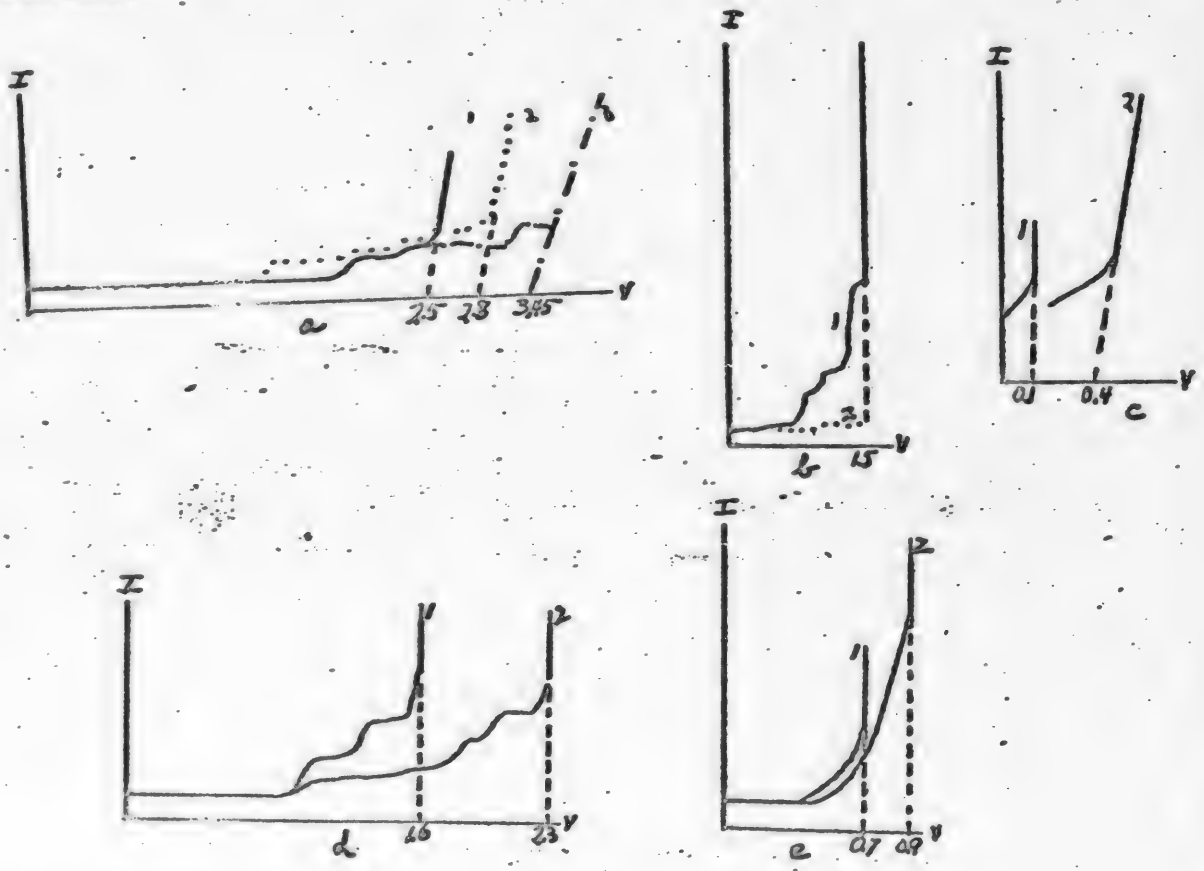

Fig. 4. Decomposition voltage of NH_4Cl at various electrodes. NH_4Cl concentration 0.1N

a) 2 mm = 0.1 volt; 4 mm = 1 division on the galvanometer scale. Electrodes: 1- Pt-steel; 2- Pt-Cu; 3- Pt-Hg. b) 1 mm = 0.1 volt; 2 mm = 1 division on the galvanometer scale. Electrodes: 1- steel-steel; 2- steel-Pt. c) 2mm = 0.1 volt; 4 mm = 1 division on the galvanometer scale. Electrodes: 1- Al-Pt; 2- Al-steel. d) Electrodes: 1- steel-Cu; 2- steel-Hg. e) Electrodes: 1- Hg-Pt, Cu-Pt; 2- Hg-steel.

1) The decomposition voltage of the aqueous solution of strychnine nitrate at platinum electrodes is 2.5 volts, while the decomposition voltage at platinum electrodes of a 0.025 N solution of ammonium chloride is 2.25 volts; thus, the decomposition voltage of strychnine nitrate is close to that of ammonium chloride;

2) The decomposition voltage of strychnine nitrate when platinum is used as the anode and other metals as the cathode, like that of ammonium chloride, is highest when platinum is used as the anode and copper or mercury as the cathode; and

3) The separation voltage of strychnine (in volts) is close to the decomposition voltage of strychnine nitrate. For instance, the decomposition voltage of strychnine nitrate is 2.5 volts at platinum electrodes, while strychnine was evolved from a 0.025 N solution of strychnine nitrate at 2.7 volts; the decomposition voltage of a 0.025 N solution of strychnine nitrate is 2.7 volts when platinum serves as the anode and mercury as the cathode, while strychnine is recovered at 2.9 volts when these electrodes are used.

Fig. 2 and Table 2 show the decomposition voltage of morphine hydrochloride and the separation voltage of morphine; Table 3 gives the formation voltages for 14 other alkaloids, while Table 4 shows the separation voltages of the following alkaloids: diacetylmorphine, papaverine, quinine, emetine, ephedrine, and salsoline.

These results indicate that:

1) The decomposition voltages of aqueous solutions of the salts of these alkaloids are close to the decomposition voltage of an aqueous solution of ammonium chloride;

2) The decomposition voltages of the above-mentioned alkaloid salts at electrodes consisting of platinum as the anode and other metals as the cathode are highest when platinum is used as the anode and copper or mercury as the cathode; and

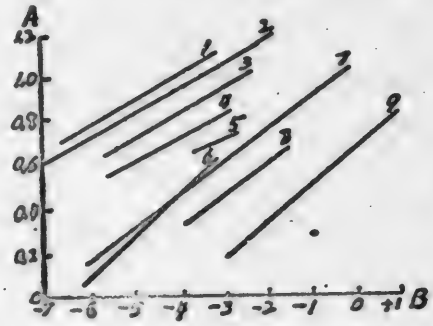

Fig. 5. Hydrogen overvoltage at various metals. Data from the Frumkin laboratory, [10].

A-Overvoltage, volts; B-log D, amp/cm^2; 1-Pb; 2-Hg; 3-Cu; 4-C; 5-Fe; 6-Ni; 7-Ag; 8-Au; 9-Pt.

3) The separation voltages of the alkaloids from their salts are lowest when aluminum serves as the anode and steel or platinum as the cathode.

Table 5 gives the melting points of the crystals recovered by electrolyzing salts of the alkaloids; they show that these crystals are the pure alkaloid bases without any impurities.

The data on the effect of the concentration of the alkaloid salts upon the decomposition voltage, given in Table 6, show that the decomposition voltage falls and then rises again when the concentration of the alkaloid salt solutions is lowered from 0.025 N to 0.001 N.

In our experiments on the effect of the cathode current density upon the magnitude of the decomposition voltage (Table 7), we found that increasing the cathode current density causes a drop in voltage to begin with, after which the decomposition voltage rises again.

SUMMARY

1. A study has been made of the decomposition voltage of ammonium chloride as

the simplest model of an alkaloid salt, using different concentrations and electrodes of different materials.

2. A study has been made of the decomposition voltages of the hydrochlorides of morphine, methylmorphine, ethylmorphine, diacetylmorphine, cocaine, quinine, emetine, salsoline, ephedrine, lodeline, papaverine, and pilocarpine; atropine sulfate; strychnine nitrate; and physostigmine salicylate.

3. The minimum voltages at which the pure alkaloid bases are recovered from their salts without any impurities have been found; these minimum voltages have been defined by us as the alkaloid separation voltages.

4. It has been shown that the decomposition voltage depends on the concentration and the current density.

5. It has been shown that the alkaloid separation voltage depends on the electrode material.

LITERATURE CITED

[1] A.Shmuk, Collected Papers on the Chemistry of Tobacco and Makhorka, 6, Krasnodar (1935).

[2] N.I.Gavrilov and A.M.Krasilnikov, Sci. Pap. Moscow State Univ., No. 3, (1934).

[3] G.Ilyin. Collected Papers on the Chemistry of Tobacco and Makhorka, 6, Krasnodar (1935).

[4] E.N.Ginsburg and N.I.Gavrilov, J. Appl. Chem., 20, 120-129 (1947).

[5] S.L.Arkhangelova, Bull. D.I.Mendeleev All-Union Chem. Soc. 1, 20-21 (1941).

[6] P.A.Shershnev and P.I.Nikozova, Med. Bull. 2, 37-41, Irkutsk (1939).

[7] P.Oficjalski, Wiadomosci Farm., 2, 37-41 (1939).

[8] M.Leblanc. Manual of Electrochemistry (1931).

[9] A.Murtazaev and A.Ablyaev, J. Phys. Chem. USSR, 14, 69 (1940).

[10] A.I.Brodsky. Physical Chemistry, p 783 (1948).

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THE PROBLEM OF AN ELECTROCHEMICAL METHOD FOR PRODUCING SODIUM PERBORATE

N. N. Drozin

In 1898 the Russian scientist Tanatar [1] produced sodium perborate, $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, for the first time by chemical and electrochemical methods. In his research on the electrochemical method he subjected a solution of borax and caustic soda to electrolysis. The resulting solution of sodium perborate was extremely weak, however. Fedotyev and Solnyshkin showed in 1915 [2] that a sufficiently highly concentrated solution of sodium perborate can be produced by electrolyzing a solution of borax and soda. At almost the same time as Fedotyev and Solnyshkin completed their research, the German scientist Arndt published his investigations of the electrolysis of soda and borax, in which he repeated the basic conclusions reached by the Russian authors.

There are two sets of equations for the anodic process that takes place at a platinum electrode when a borax-soda solution is electrolyzed: one has been put forward by Foerster [3], and the other by Arndt [4].

According to Foerster, sodium percarbonate is evolved at the anode. Decomposed by water, it forms hydrogen peroxide as follows:

$$Na_2C_2O_6 + 2H_2O = 2NaHCO_3 + H_2O_2, \quad (1)$$

the latter combining with the metaborate and water:

$$NaBO_2 + H_2O_2 + 3H_2O = NaBO_2 \cdot H_2O_2 \cdot 3H_2O. \quad (2)$$

This yields the sodium perborate.

According to Arndt, the electrochemical process for producing sodium perborate begins with the formation of a higher oxide of platinum, PtO_3, which oxidizes the sodium metaborate $NaBO_3$, to the sodium salt of perboric acid. The reaction occurring at the anode is:

$$NaBO_3 + H_2O = NaBO_2 \cdot H_2O_2. \quad (3)$$

According to Foerster [5], the hydrogen peroxide formed during the electrochemical process for the production of sodium perborate decomposes in part, owing to the following reactions:

$$Pt + 3H_2O_2 = PtO_3 + 3H_2O; \quad (4)$$

$$PtO_3 + H_2O_2 = PtO_2 + O_2 + H_2O. \quad (5)$$

The chemical decomposition of the hydrogen peroxide may be paralleled by its electrochemical decomposition, say, as:

$$H_2O_2 = O_2 + 2H^+ + 2\underline{e} \quad (6)$$

Lastly, mention should be made of the loss of H_2O_2 as a result of cathodic reduction.

The present paper has as its topic an investigation of the decomposition of hydrogen peroxide (free or bound to the sodium perborate) during the electrolysis of soda and borax in the presence of various additives, or without them.

EXPERIMENTAL*

The apparatus for the electrochemical production of sodium perborate is shown in Fig. 1.

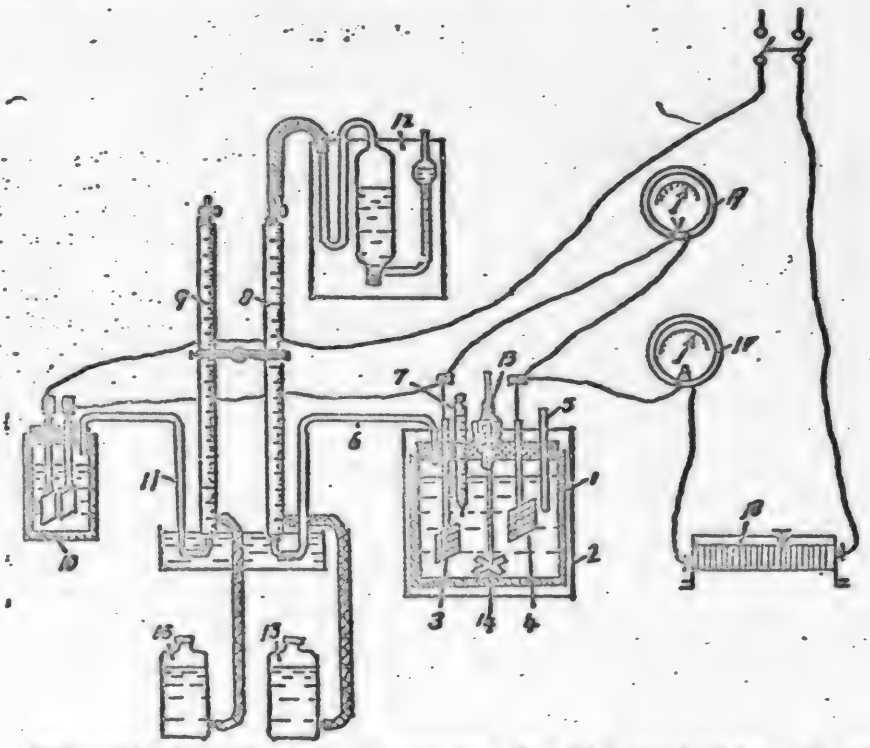

Fig. 1. Schematic layout of the apparatus for the production of sodium perborate.

The electrolyzer 1, with a capacity of 1.5 liters, is placed in thermostat 2, and hermetically sealed with a stopper, which serves as a support for the reticular electrodes: platinum anode 3, and nickel cathode 4. The area of the platinum mesh (784 openings per cm^2) is 5.3 cm^2 (allowing for the surface of the platinum alone).

The nickel mesh was prepared from platelets 2 mm wide. It has 4 joints per cm^2 of mesh. The area of the nickel mesh is 20 cm^2 (allowing for the surface of the platinum alone).

*M. M. Katasonova assisted in performing the experiments.

The nickel mesh was prepared from platelets 2 mm wide. It has 4 joints per cm^2 of mesh. The area of the nickel mesh is 20 cm^2 (allowing only for the nickel surface). The electrodes are spaced 1.5 cm apart.

Besides the electrodes, the stopper carries a tube 5 for taking samples of the solution, a tube 6 for drawing off gas to a buret 8, and a thermometer 7. The electrolyte is stirred by means of a wooden stirrer 14, fitted with a mercury seal 15. The mixture of gases passes from the coulometer 10 through tube 11 to buret 9. Buret 8 is connected to a Hempel gas buret 12, which absorbs oxygen. Bottles 13 and 16 serve to level out the volumes of gas in burets 8 and 9.

The current, measured by the ammeter 17, is regulated by rheostat 18. The voltage across the electrodes is measured by means of voltmeter 19.

The experiment was performed as follows. One liter of solution containing 120 g of soda and 30 g of borax was poured into the electrolyzer vessel. As soon as the current is turned on, oxygen and hydrogen are liberated vigorously.

Burets 8 and 9 are filled with water, and tubes 6 and 11 are inserted underneath them. After the burets are filled with gas, the oxygen-hydrogen mixture in buret 8 is transferred to the Hempel gas buret. The degree of anodic oxidation and the amount of H_2O_2 reduction at the cathode are computed from the losses of oxygen and hydrogen in the electrolyzer gas.

The concentration of sodium perborate is determined by acidulating 1 ml of the electrolyte with dilute (1:3) sulfuric acid and then titrating back with 0.1 N $KMnO_4$. The amount of hydrogen peroxide found is converted in terms of sodium perborate. The current efficiencies are determined from the actual percentage of active oxygen, as against the quantities computed from Faraday's law.

The borax-soda solution was electrolyzed under the following conditions: current 8.0 amp; voltage across the electrodes 7 volts; electrolyte temperature 13-16°; and current density 1.6 amp/cm^2 (in terms of the platinum surface).

The current efficiency drops to zero after 2 hours of electrolysis (Table 1). This is due chiefly to the circumstance that the quantity of free oxygen evolved at the anode rises with an increase in the concentration of sodium perborate. Only 6-10% of the current is used for cathodic reduction.

TABLE 1

Results of the Electrolysis of Borax and Soda at a Dense Platinum mesh

Time, min.	Anodic oxidation, %	H_2O_2 concentration, g/liter	Sodium perborate conc. g/liter	Reduction of H_2O_2 at the cathode, %.
5	45.8	-	-	5.9
37	30.9	1.19	5.4	6.9
79	16.2	1.71	7.75	9.7
124	0	2.07	9.4	9.8

We then examined the effect of various additives upon the rate of decomposition of hydrogen peroxide during the electrolysis of a soda-borax solution.

The following additives were introduced into the solution: potassium fluoride (1 g/liter); potassium sulfate (50 g/liter); boric acid (30 g/liter); sodium bicarbonate (20 g/liter); monometallic sodium phosphate (15 g/liter); and lithium chloride (15 g liter).

The drop in current efficiency is slowed down by the presence of the additives causing the terminal concentration of sodium perborate to rise (Fig. 2). The concentration of sodium perborate rises most of all when boric acid (Curve 1) or sodium bicarbonate (Curve 2) is present. The effect of potassium fluoride (Curve 3)

is like that of sodium bicarbonate during the middle of the process; but toward the end, the former's action is weaker than the latter's. Potassium sulfate (Curve 4), sodium phosphate (Curve 5), and lithium chloride (Curve 6) behave almost identically alike, exerting little effect upon the terminal concentration of sodium perborate.

The change in the concentration of sodium perborate when no additive is present is shown for the sake of comparison (Curve 7).

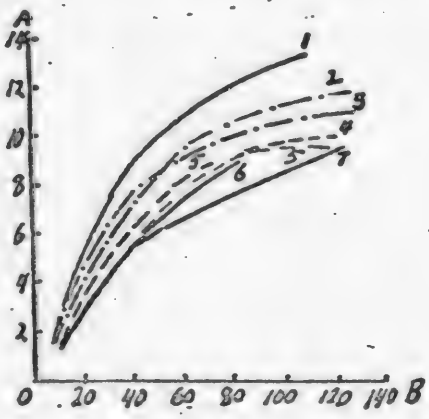

Fig. 2. Effect of various additives upon the concentration of sodium perborate in the electrolyte.

A- Concentration of sodium perborate, g/liter); B- time, minutes. Additives. 1-boric acid, 2-sodium bicarbonate; 3-potassium fluoride; 4-potassium sulfate; 5-sodium phosphate; 6-lithium chloride; 7-without any additive.

We then investigated the way in which the loss of hydrogen peroxide varies with the concentration of H_2O_2 present at any given instant; this refers to the total amount of hydrogen peroxide present in the solution, whether free or bound to the sodium perborate. We used the results of the experiments in which we determined the total quantity of H_2O_2 at various instants during electrolysis.

Let C_1 be the concentration of H_2SO_4 at the given moment of electrolysis, and C_2 the concentration of H_2O_2 that might be formed theoretically during the interval $t_2 - t_1$. Thus, the H_2O_2 concentration in the solution after t_2 minutes (after the start of electrolysis) should equal $C_1 + C_2$, provided that no hydrogen peroxide is decomposed during this interval of time. But in actuality, hydrogen peroxide is decomposed during electrolysis. The experimental concentration of H_2O_2 within t_2 minutes after the start of electrolysis, C_3, will always be less than the theoretical concentration $C_1 + C_2$.

Let A denote the loss of hydrogen peroxide during the time interval $t_2 - t_1$. Then $A = C_1 + C_2 - C_3$. We found experimentally that:

$$\frac{A}{C_1 + C_2} = K, \qquad (I)$$

where K is a constant.

Whence:

$$A = KC_1 + KC_2. \qquad (II)$$

When the current is constant, the second term in Equation (II), KC_2, remains constant. Let us call it K_1. The final form of Equation (II) then becomes:

$$A = K_1 + KC_1. \qquad (III)$$

As Equation (III) indicates, the losses of hydrogen peroxide are directly proportional to C_1, the total H_2O_2 at the given instant of electrolysis.

If we plot the total concentration of hydrogen peroxide at various electrolysis times t_0, t_1, t_2, t_3, along the axis of abscissas, and the losses of hydrogen peroxide at the identical succeeding time intervals $t_1 - t_0$, $t_2 - t_1$, $t_3 - t_2$ (this interval was 30 minutes in our tests), the change in the losses of H_2O_2 as a function of the concentration of H_2O_2 is represented by straight lines (Fig. 3).

The start of the straight lines (i.e., the intersections of Curves 1-5 with the dotted line aa_1) indicates the losses of hydrogen peroxide during the first 30

minutes of electrolysis. When no additive is used, the losses are a maximum at the start of electrolysis (Line 1). When LiCl (Line 2), KF (Line 3), $NaHCO_3$ (Line 4), or H_3BO_3 (Line 5) is added, the losses drop; at the same time the total concentration of hydrogen peroxide rises.

The intersections of the dotted curves bb_1 and cc_1 with the straight lines 1-5 indicate the losses of hydrogen peroxide at various H_2O_2 concentrations for the second and third 30 minutes of electrolysis, respectively.

Let us compare Line 1 (without additive) and Line 5 (with boric acid added). Points a and a_1 indicate that the losses of hydrogen peroxide during the first 30 minutes have been cut in half by the addition of boric acid. The effect of adding H_3BO_3 is much weaker during the second 30 minutes (points b and b_1), while the losses of hydrogen peroxide are practically unchanged by the addition of boric acid during the third 30 minutes (points c and c_1). The same pattern of behavior is exhibited by the other additives.

It should be noted that when additives are used during electrolysis, the concentration of hydrogen peroxide rises, and as a result its decomposition rate rises as well.

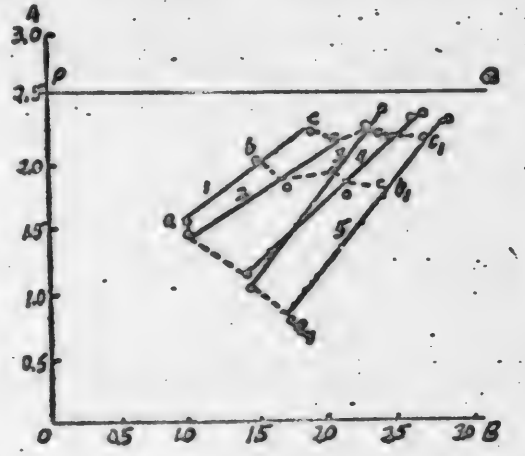

Fig. 3. Effect of additives upon the decomposition of hydrogen peroxide during electrolysis.

A- H_2O_2 losses, grams; B- total H_2O_2 concentration, g/liter. Additives: 1- no additive; 2- LiCl; 3- KF; 4- $NaHCO_3$; and 5- H_3BO_3.

Losses of hydrogen peroxide (at various concentrations): a and a_1 - during the first 30 minutes of electrolysis; b and b_1 - during the second 30 minutes; c and c_1 - during the third 30 minutes.

For instance, 0.5 g more of H_2O_2 is lost during the second 30 minutes than during the first when electrolysis is effected without additives, whereas when boric acid is added, the difference between the losses in these intervals of time is 1.04 g of H_2O_2, i.e., more than double. Lastly, more is lost during the third 30 minutes than during the second: 0.35 g more when boric acid is added, and 0.20 g more when it is not added. The same holds true for the other additives.

The stabilizing effect of the various additives is exhibited most strongly during the first 30 minutes of electrolysis. Later on, the rate of decomposition of the hydrogen peroxide rises when additives are present, owing to the increase in the concentration of H_2O_2; but the rate remains lower than the decomposition rate with no additive present throughout the electrolysis period; only toward the end of the process does it approach it.

Hence, additives promote the accumulation of hydrogen peroxide in the electrolyte.

This may be illustrated by the following example: The effect of adding H_3BO_3 upon the decomposition of the hydrogen peroxide resulted in increasing the H_2O_2 concentration, to 2.75 g/liter after 90 minutes of electrolysis, instead of the 1.75 g/liter obtained during electrolysis with no additive present. But by this time, the current efficiency becomes negligible.

The PQ line, parallel to the axis of abscissas, intercepts a section of the

ordinates axis that denotes the quantity of hydrogen peroxide that could be formed theoretically after 30 minutes of electrolysis. As the process draws to a close, the straight lines 1-5 approach the line PQ; in other words, the current efficiency approaches zero.

50 ml of perhydrol, containing 13 g of H_2O_2, was added to 1 liter of electrolyte in order to ascertain the effect of an excess of hydrogen peroxide upon the current efficiency. After electrolysis was over a deposit of sodium perborate, containing 10% of active oxygen, was found at the bottom of the electrolyzer. The deposit weighed 16.55 g. The figures in Table 2 indicate that the hydrogen peroxide is strongly decomposed chemically during electrolysis.

In fact, the amount of oxygen evolved in the electrolyzer during 5, 35, and 90 minutes exceeds the amount of oxygen obtained in the coulometer by 29.8, 27.7, and 3.4 cm^3.

Moreover, as the concentration of the hydrogen peroxide rises, cathodic reduction increases sharply.

Thus, the chemical decomposition of hydrogen peroxide, as well as the phenomenon of cathodic reduction, and its electrochemical decomposition, all prevent an appreciable accumulation of hydrogen peroxide during the electrolysis of a soda-borax solution.

TABLE 2

Decomposition of Hydrogen Peroxide During Electrolysis

Time, Minutes	Coulometer gas: Total gas, cm^3	Coulometer gas: H_2, cm^3	Coulometer gas: O_2, cm^3	Electrolyzer gas: Total gas, cm^3	Electrolyzer gas: H_2, cm^3	Electrolyzer gas: O_2, cm^3	Cathodic reduction, %
5	86.8	57.8	29.0	98.2	39.5	58.7	31.7
35	81.9	54.6	27.3	100.0	45.0	55.0	17.6
90	97.6	65.0	32.6	94.6	59.2	35.4	8.0

In our subsequent experiments we used a platinum mesh with 4 juntions per cm^2, manufactured from wire 0.3 mm in diameter. The platinum area was 1.8 cm^3. The nickel cathode was replaced by a smaller one, with an area of 8.6 cm^2. The electrolysis conditions were as follows for the first experiment: current 3 amp; voltage across the electrodes 7 volts; anode current density D_{an} = 1.65 amp/cm^2. In subsequent experiments the current was 6 amp, and the voltage across the electrodes 9-10 volts. The volume of the electrolyte was 600 ml in all the experiments.

The change in the concentration of the sodium perborate during electrolysis is shown in Fig. 4. Curves 1 and 2 show the rise in concentration during electrolysis with no additive present (current densities 1.65 and 3.3 amp/cm^2, respectively).

In one of the tests, 10 g of solid sodium perborate was added to 600 ml of the electrolyte, 4.1 g entering into solution. The effect of adding the sodium perborate is shown by Curve 3.

When borax is added until it settles out in the solid phase, the final concentration of sodium perborate rises considerably, compared with the concentration obtained without an additive (Curve 4).

The effect of the concentration of hydrogen peroxide upon the losses of the same is shown in Fig. 5. Straight lines 1 and 2, parallel to each other, indicate the experimental results for anode current densities of 1.65 and 3.3 amp/cm^2, respectively. An increase in the current density produces a rapid rise in the rate of

decomposition of the hydrogen peroxide. At the same time, the actual percentage of free oxygen remains nearly unchanged. As before, the straight lines PQ and P_1Q_1 intercept a section of the ordinates axis that indicates the quantity of hydrogen peroxide that could be produced theoretically within 30 minutes of electrolysis for currents of 6 and 3 amp, respectively.

The presence of sodium perborate in the bottom phase (Line 3) promotes an increase in the concentration of hydrogen peroxide during the first 30 minutes, owing to its entrance into the liquid phase. As electrolysis proceeds, the rate of decomposition of the hydrogen peroxide rises sharply.

When borax is present in the bottom phase (Line 4), the decomposition of hydrogen peroxide is sharply reduced during the first 30 minutes; at the same time the actual percentage of H_2O_2 rises. This is seen by comparing points a_1 and a_2 on Lines 2 and 4.

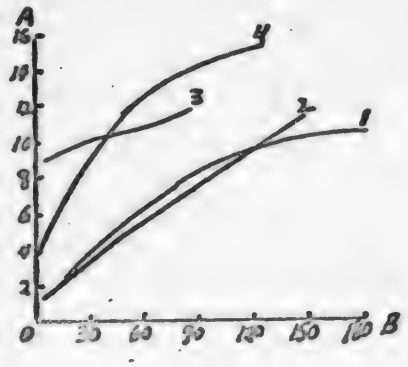

Fig. 4. Effect of additives and current density upon the concentration of sodium perborate in the electrolyzer.

A-Perborate concentration, g/liter; B-Time, minutes. Additives: 1-without an additive, current density 1.65 amp/cm^2; 2-without an additive, current density 3.3 amp/cm^2; 3-solid sodium perborate; 4-borax.

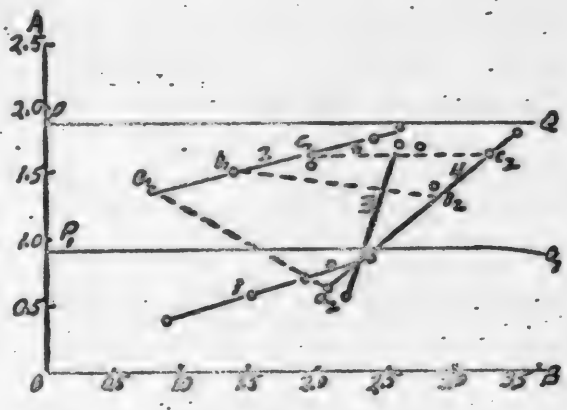

Fig. 5. Effect of additives and current density upon the decomposition of hydrogen peroxide during electrolysis.

A - H_2O_2 losses, grams; B- total H_2O_2 concentration, g/liter. Anode current density: 1 - 1.65 amp/cm^2; 2-3.3 amp/cm^2. Additives: 3-sodium perborate; 4-borax.

But as the concentration of hydrogen peroxide rises, its losses rise faster when borax is present than during electrolysis without an additive present.

SUMMARY

1. A study has been made of the decomposition of hydrogen peroxide (bound to sodium perborate or free) during electrolysis of a soda-borax solution. It has been shown that the rate of decomposition of the H_2O_2 is directly proportional to its total concentration.

2. Additions of potassium fluoride, potassium sulfate, boric acid, sodium bicarbonate, monometallic sodium phosphate, lithium chloride, and borax, promote an increase in the total concentration of hydrogen peroxide.

3. The effect of additives upon the decomposition of hydrogen peroxide depends upon the stage of electrolysis.

LITERATURE CITED

[1] Tanatar, Z. physik. Chem., 26, 132 (1898).

[2] P.P.Fedotyev and V.Solnyshkin, Coll. Res. Papers, 104 (1936).

[3] F.Foerster, Z. angew. Chem., 34, 354 (1921).

[4] K.Arndt u. E. Hantge, Z. Elektrochem., 28, 263 (1922).

[5] F.Foerster, Z. physik. Chem., 69, 254 (1909).

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A METHOD OF SYNTHESIZING ESTERS OF ORTHOSILICIC ACID

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The most valuable practical method of producing the esters of orthosilicic acid is based upon the reaction of silicon tetrachloride with alcohols [1,2], as follows: $SiCl_4 + 4ROH \rightarrow Si(OR)_4 + 4HCl$. This reaction, discovered by Ebelmen [1], was first studied in detail by D.I.Mendeleev [3,4], who noted that is is accompanied successively by exothermic and endothermic effects, due to two parallel processes - chemical and physical. The latter process is marked by a marked drop in the temperature, caused by the formation of gaseous HCl. D.I.Mendeleev was also the first to establish the correct structure of ethyl orthosilicate, assigning it the formula $(C_2H_5)^4Si^2O^4$, considering Si^2 silicon to be the true tetra-atomic radical.

Further work was done on the development of this method of producing esters of orthosilicic acid from $SiCl_4$ and alcohols by Soviet authors [1,2,5-8]. These authors, and other researchers, showed that the reaction of $SiCl_4$ with an alcohol is accompanied by side reactions, which cause the yields of ortho esters to be extremely low if precise conditions for the synthesis are not strictly observed. In order to secure satisfactory yields of the esters of orthosilicic acid, conditions for their synthesis from $SiCl_4$ and alcohols were discovered (which are generally accepted at the present time), in which the effect of side reactions is reduced to a minimum. These conditions are as follows: nothing but absolute alcohols are employed; the reaction is carried out at as low a temperature as possible, down to -80° [8] often with solvents present [5,7], the $SiCl_4$ is added to the alcohol as slowly as possible; and the HCl evolved during the reaction is driven off in a stream of dry air or CO_2. Compliance with all these conditions, however, makes this method of producing orthosilicic esters very inconvenient, long drawn out, and laborious. Moreover, when methyl orthosilicate is synthesized even under these conditions, the yield remains low, amounting to no more than 60-70% at best.

The method we have developed for synthesizing esters of orthosilicic acid is based upon the reaction of silicon tetrachloride with alcohols, performed under conditions that are diametrically opposite to those cited above; this method is distinguished from present methods by its simplicity and rapidity and excels them in the yield of the end product, especially in the synthesis of $Si(OCH_3)_4$. A major advantage of this method is the feasibility of using alcohols that contain a few per cent of water, which is removed by the action of the silicon tetrachloride itself.

This is especially important in the case of ethyl alcohol, inasmuch as it enables one to use 96% alcohol - rectified alcohol - thus eliminating the necessity for dehydrating it by any of the customary methods.

All the side reactions that lower the yield of esters of orthosilicic acid are due to the formation of polysiloxane polymers as the result of the hydrolysis of $SiCl_4$, chloro ortho esters, and ortho esters by water, either present in the original alcohol or formed during the reaction by the interaction of the alcohol with hydrogen chloride. Thus, the sole condition required for successful synthesis, besides the absence of water in the original alcohol, is the prevention of its formation during the reaction. To effect this, in the present method the silicon tetrachloride is added as rapidly as possible to the absolute alcohol, which is taken in slight excess. This is done in order to provide as large an excess as possible of silicon tetrachloride and chloro ortho esters in the reaction mixture, since we know that alcohols react much more readily with them than with hydrogen chloride. Moreover, the reaction of $SiCl_4$ with an alcohol is not carried out in the cold, resulting in the dissolution of a tremendous quantity of HCl (which, by the way, is unnecessary, since the reaction is markedly endothermic after 1/3 to 1/2 the $SiCl_4$ has been added), but, on the contrary, with the application of vigorous heating and stirring, causing the quantity of hydrogen chloride retained in the reaction mixture to remain at a minimum.

The water, if any, in the original alcohol is eliminated by the action of $SiCl_4$, it being added to the alcohol in sufficient quantity to bind any water that may be present; the anhydrous alcohol containing the hydrogen chloride being driven off later. The alcohol thus dehydrated enters into reaction at once.

The yield of esters of orthosilicic acid exceeds 80% in the present method of synthesis.

EXPERIMENTAL

Methyl ester of orthosilicic acid. 3 ml of $SiCl_4$ is added to 200 g of methanol, with a b.p. of 64.5° (752 mm), after which the alcohol is distilled, the first 3 ml of the distillate being discarded. The resulting 184 g of anhydrous alcohol, with a b.p. of 64-66°, containing some HCl, is placed in a three-necked, round-bottomed flask, fitted with a high-efficiency mechanical stirrer, a dropping funnel, and a high-capacity reflux condenser, terminating in a wash bottle containing concentrated H_2SO_4, and heated to boiling. 238 g (1.4 mol) of silicon tetrachloride, with a b.p. of 57.0° (760 mm) is added, as rapidly as possible (within 40 minutes), to the boiling alcohol, with vigorous heating and stirring. After all the $SiCl_4$ has been added, heating and stirring are continued for another 30 minutes, after which the reaction mixture is distilled. 17.5 g of methanol containing HCl passes over at 64-66°; this may be employed in later syntheses. The yield of methyl orthosilicate, with a b.p. of 118-121°, is 172.5 g, or 81% of the theoretical, based on the $SiCl_4$ taken for the reaction. The constants of the ortho ester are as follows: B.p. 121.0°(761 mm); d_4^{20} 1.033; n_D^{20} 1.3681, after it has been treated with a small quantity of sodium methylate and then distilled into a column.

Ethyl ester of orthosilicic acid. 13 ml of $SiCl_4$ is added to 200 g of 96% ethyl alcohol, with a b.p. of 78° (760 mm), after which the alcohol is distilled, the first four ml of the distillate being discarded. This yields 150 g of anhydrous alcohol, containing HCl, with a b.p. of 77-81°, which is then transferred to the apparatus described above. The alcohol is heated to boiling, and 127.5 g (0.75 mol) of $SiCl_4$ is added as quickly as possible (within 20 minutes), with intensive stirring and the heat turned off. After 1/3 of the $SiCl_4$ has been added, the reaction mixture is intensely heated during the addition of the rest. When all the $SiCl_4$ has been added, the reaction mixture is heated and stirred for another 30

minutes, after which it is distilled. The output of ethyl orthosilicate, with a b.p. of 164-167°, is 130 g, or 83% of the theoretical, based on the $SiCl_4$ taken for the reaction. Moreover, 15.5 g of ethyl alcohol containing HCl, with a b.p. of 80-83°, is recovered, which is employed in subsequent syntheses. The constants of the ortho ester are as follows:

B.p. 165.3° (761 mm); d_4^{20} 0.9346; n_D^{20} 1.3831.

after treatment with a small amount of sodium ethylate and distillation into a column.

LITERATURE CITED

[1] B.N.Dolgov. The Chemistry of Organosilicon Compounds, 77, United Scientific and Technical Press, Leningrad (1933).

[2] K.A.Andrianov, Prog. Chem., 18, 151 (1949).

[3] D.I.Mendeleev, Chem. Jour. 4, 65 (1860).

[4] D.I.Mendeleev, Principles of Chemistry, II, 453. United Scientific and Technical Press, Moscow-Leningrad (1934).

[5] M.N.Kalinin, Doklady (Bulletin) Akad. Nauk. USSR, 18, 431 (1938).

[6] K.A.Andrianov. Doklady (Bulletin) Akad. Nauk. USSR, 28, 66 (1940).

[7] I.V.Grebenshchikov and assoc. Transluscent Optics, 145. United State Publishing House, Moscow, Leningrad (1946).

[8] A.P.Krenkov and G.D.Nesmeyanova, J.Gen.Chem. 19, 660 (1949).*

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THE PROBLEM OF THE COLOR OF POLYMER RESINS IN A FINELY DISPERSED STATE AND THE SELECTIVE ADSORPTION OF COLORS BY SYNTHETIC RESINS

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As we know, articles of everyday use made of plastics (or other materials, for that matter) have to meet high standards of form and beauty of coloring. Components designed for architectrual or decorative use must also be designed artistically and beautifully colored.

Color is employed not only for articles of everyday use or decorative articles, however; it is also employed in technical parts, such as steering wheels and levers for automobiles and airplanes, cases for control or measuring instruments, knobs for instruments of various kinds, etc. Various kinds of colored organic glass, used as light filters, signal glass, etc., have been introduced during the last few years.

In spite of the great practical importance of color in synthetic resins and plastics, not much work has been done on the chemistry or technology of this process.

Even less is known of the physical and chemical principles underlying the process. The achievements of science and technology in the dyeing of textiles cannot be fully applied to the tinting of synthetic resins and plastics, owing to the peculiar chemical composition and properties of the latter, as well as the conditions governing their molding into articles, which usually involve the use of high temperatures and pressures.

Celluloid and galalith were the first plastics to be colored. For a long time these two of the oldest plastics were outstanding in the beauty and diversity of their tinting. Recently, considerable progress has been made in the tinting of plastics, involving acetylcellulose, the acetopropionates, acetobutyrates, and ethers of cellulose, and the phenol-formaldehyde resins.

The development of tinting methods and the selection of the corresponding dyes for polymer resins and plastics, which are employed widely in industry, has come to the fore of late. This is mainly true of polymethyl methacrylate, polystyrene, polyvinyl acetate, polyvinyl chloride, and various of their copolymers. Despite the importance of this problem, the literature on the coloring of polymer resins is quite scanty. Most of the published papers deal with the tinting of phenol aldehyde plastics. This includes the papers by Kozlova, Neubauer, and

Gvozdeva [1], Falkina [2], Yefimova [3], Simanovskaya [4], Petrov and Grigoryev [5], and Osmina [6].

The phenol-formaldehyde resins themselves are yellowish-brown, the intensity of the color increasing with time, which is why we believe it is unlikely that the methods of tinting typical (unmodified) phenol-aldehyde plastics will be appreciably improved in the near future.

The outlook is very much better for another group of condensation resins: the amino-plasts.

With the appearance of polymer resins on the market, the research institutes and industrial laboratories set atout the development of methods for tinting this group of resins. In 1944, the Committee on Architecture commissioned the laboratory of Plastics Technology of the D.I.Mendeleev Institute to do research on the tinting of blocks (or sheets) or polymethyl methacrylate, with a view toward their utilization as decorative materials and finishes in building construction. Investigation of the light fastness of various dyes, involving exposure of tinted samples to light indoors for four years, indicated that the samples tinted with basic and sudan dyes were light fast. During this period most of the dyes tested were bleached out or faded considerably.

The coloring of the surface of polymethyl methacrylate products with alcoholic solutions of dyes, employed by us at that time and now used industrially, has one major disadvantage, notwithstanding its simplicity and convenience: the dye does not penetrate very deep and is easily removed when the tinted products are machined with a cutting tool. Parts of this type can stand only light buffing and polishing. In spite of this handicap, our research on the surface tinting of a polymethyl metacrylate block has shown that basic dyes – contrary to expectation – proved to be lightfast when applied to the surface of a polymethyl methacrylate. But we were unable to provide a satisfactory explanation for the fastness to light of the basic dyestuffs and the inadequate fastness of most of the acid dyes we tested. This phenomenon became clear as the result of our further research, which is reported below.

In contrast to surface tinting, dyeing plastics through and through does not possess these defects, but it is hard to perform for polymethyl methacrylate and other polymer plastics. The difficulty involved in tinting block and emulsion polymers is that most organic dyes (with the exception of the rather inaccessible sudan dyes) dissolve with difficulty in monomeric organic compounds, whereas many of those that do dissolve are either decolorized or change color under the action of temperature or the oxidizing action of the peroxides employed as catalysts. Moreover, some dyes are inhibitors, retarding the polymerization reaction (brilliant green, malachite green, methylene heliotrope, etc.). Only few organic dyestuffs yield satisfactory results (such as, rhodamine, auramine, and safranine); we confirmed this by testing a large number of different dyes. This is obviously the reason for the poor assortment of colored block and emulsion polymers put out by the plastics industry. They include almost no items colored green, blue, brown, black, light blue, violet, or other tints with organic dyestuffs.

Mineral pigments exhibit much higher fastness to light and resistance to various chemical reagents. But, their high specific gravity makes it hard to keep them in a state of suspension during a process of polymerization (this is particularly true of block polymerization) that requires a long time, during which much of the pigment may settle out. Using a pigment that is finely ground and carefully sifted

through an extremely fine screen (10,000 holes per cm^2) makes it possible to produce a beautiful, even tint of block polymethyl methacrylate or polystyrene.

EXPERIMENTAL

Not securing satisfactory results in tinting block and emulsion polymers of methyl methacrylate with organic dyestuffs for the reasons cited above, we decided to by-pass these difficulties in another way. We did this by coloring the ready polymer, in a finely dispersed state, with water-soluble, chiefly basic, dyes. The latter attracted our attention because of their brilliance, their high solubility in water, and their availability, inasmuch as they are produced by domestic industry on an industrial scale. We assumed that the polymer particles produced by dispersion in water are so small (0.1-0.3 micron [8]) as to be completely dyed by aqueous solutions of organic dyestuffs, notwithstanding the latter's hydrophobic nature (the harmful effect of a peroxide upon the dye is completely eliminated in this procedure).

In fact, our presupposition proved to be correct: we obtained the finest powders of polymethyl methacrylate, polystyrene, and other polymers, tinted in all shades. We also discovered an extremely interesting phenomenon: only basic dyes yielded completely stable colors. Acid and direct dyes tinted the polymer, to be sure, but they were completely washed out of it by water. For a long time this selective sorption of the basic dyestuffs by polymethyl methacrylate and other polymers remained a riddle to us. Not only did the basic dyes tint the polymer particles permanently and well, but they produced aggregation, as a result of which all the polymer settled out as a deposit upon standing. Complete coagulation took place, however only when the amount of basic dye placed in solution reached a certain value.

As for the acid, direct, and sudan dyes (sudan 4), they cause absolutely no coagulation of the dispersed polymer at any concentration whatsoever. All this pointed to the specific action of the basic dyestuffs and justified the assumption that emulsion polymers are acidic.

We found no direct references in the literature to the acidic nature of emulsion polymers. Only Morgan [9], in his study of the kinetics of polymerization of some unsaturated compounds with ammonium persulfate present, expressed the supposition that the polymerization reaction is apparently accompanied by another side reaction, which, he believed, involved the oxidation of the monomer. It is quite obvious, however, that all the conditions are present for an oxidation reaction during polymerization, since the latter is usually performed in the presence of such initiators as benzoylperoxide, hydrogen peroxide, and other peroxides, which are markedly oxidative, and the unsaturated compounds themselves tend toward oxidation.

To check this assumption, we made a determination of the acid numbers of various polymers produced by emulsion polymerization in the presence of ammonium

persulfate and benzoyl peroxide. Our experiments confirmed our assumptions: all the polymers of styrene, methyl methacrylate, polyvinyl acetate, and polyvinyl chloride proved to be acidic. Moreover, the acidity of the polymers was a direct function of the amount of (oxidative) initiator used in polymerization.

Prolonged treatment of the emulsion polymers with steam (for 6 hours), repeated reprecipitation from an aqueous solution of acetone, and fractionation lowered the polymers' acid number appreciably, but did not enable us to make them completely neutral. In every case some acid number remained, with 2 carboxyl groups, on the average, per mol of the polymer.

The research was done with methyl methacrylate, styrene, and a copolymer of methyl methacrylate and vinyl acetate. The methyl methacrylate and the styrene were polymerized in an aqueous medium, ammonium persulfate being employed as the initiator for the former, and benzoyl peroxide with some ammonium persulfate added serving as the initiator for the latter. The polymers were precipitated with hydrochloric acid.

To make sure that all the mineral acids were removed during washing, the dried polymers were tested for their chlorine and sulfur content by fusing them with metallic potassium. The sample showed that there was no trace of these elements in the emulsion polymers (styrene and methyl methacrylate).

Table 1 lists the data on the determination of the acid numbers and other constants of polymethyl methacrylate and polystyrene at the start and after repeated reprecipitation or fractionation.

As the quality of ammonium persulfate was increased from 2.5% to 3.5%, the acid number of the polymer rose from 2.06 to 3.93, all other conditions in the polymerization of methyl methacrylate being equal.

When such a polymer was fractionated from an acetone solution by successively precipitating the various fractions by adding different quantities of water, we

TABLE 1

Results of the Analysis of Polymethyl Methacrylate and Polystyrene Before and After Fractionation

Polymer	Acid number	Molecular weight	Number of carboxyl groups per mol of polymer
Polymethyl methacrylate			
Original	2.08	100000	3.7
1st fraction	1.93	146000	2.7
2nd fraction	1.08	123000	2.2
3rd fraction	0.79	128000	1.8
4th fraction	1.09	–	–
5th fraction	1.08	–	–
Polystyrene, original	14.1	–	–
After first reprecipitation.	7.65	–	–
" 2nd "	5.3	–	–
" 3rd "	3.27	–	–
" 4th "	3.15	–	–
" 5th "	3.15	34000	1.9

got five fractions of polymethyl methacrylate, the characteristics of which are given in Table 2. Table 2 shows that as the quantity of ammonium persulfate is increased, the acid number of the original polymer rises while the molecular weight falls.

TABLE

Results of the Analysis of the Various Fractions of Polymethyl Methacrylate Produced by Emulstion Polymerization in the Presence of 3.5% Ammonium Persulfate

Fraction Number	Acid Number	Molecular weight of the polymethyl methacrylate	Number of carboxyl groups per mol of the polymer
1	1.25	115000	2.6
2	1.08	106000	2.04
3	1.17	96600	2.02
4	1.21	87400	1.9
5	1.0	86000	2.7

To ascertain whether emulsion polymethyl methacrylate enters into a reaction when colored with basic dyestuffs in equimolecular proportions, and whether this is in any way related to the polymer's acid number, we tested the tinting of the polymers, with quantitative determinations of the amount of the dyestuff used.

It has been noted above that adding a certain quantity of dyestuff to a polymer in suspension causes the latter to coagulate and settle out as a precipitate. During this process much of the dyestuff is absorbed by the polymer, while the remainder staying in solution changes its initial hue slightly. This is apparently due to the fact that when salts of basic dyestuffs react with an acid polymer, an equivalent quantity of a mineral acid is evolved (HCl, H_2SO_4), which, in turn, produces a change in the hue of the unreacted basic dyestuff.

These experiments were performed as follows: a 5% solution of the basic dye (crystal violet), containing 0.3028 g of the dry dyestuff, was added to 100 ml of a suspension of polymethyl methacrylate, containing the requisite quantity of the polymer. The polymer that was thrown down during dyeing was filtered out on a Buchner funnel and washed with distilled water until the filtrate was colorless. The mother liquor was combined with the wash waters and analyzed for its residual dyestuff by means of a Dubosq colorimeter, using a standard solution of the same dyestuff, prepared by dissolving 0.0126 g of crystal violet in 1 liter of distilled water, for comparison.

An equivalent quantity of sulfuric or hydrochloric acid was added to the standard solution, to eliminate errors in finding the amount of dyestuff that reacted with the polymer, due to a change in the hue of the dyestuff in the filtrate during the colorimetric determination. These experiments yielded the following results:

38.2471 g of emulsion polymethyl methacrylate, with a molecular weight of 96,600, absorbs 0.3543 g of the dyestuff crystal violet (molecular weight 407) from solution. Thus, 1 mol of the polymer requires 2.1 mols of the dyestuff when the polymer is dyed with an excess of crystal violet.

Table 3 below gives the detailed figures on the dyeing of 100 ml of an aqueous suspension of polymethyl methacrylate with various quantities of the same dyestuff, with quantitative determination of the consumption of the latter.

When dyed with basic dyestuffs (crystal violet) the polymethyl methacrylate coagulates and settles out of an aqueous suspension only when the concentration of dyestuff in the solution reaches a certain value (1 mol of the polymer requires 2

mols of the basic dyestuff), as we see in Table 3. Increasing the quantity of dyestuff beyond this level causes no essential change. When the quantity of dyestuff in solution falls below this level, the polymer does not settle out at all or is only partially coagulated, the previous molar proportions no longer holding good (one mol of dyestuff per mol of the polymer). To make even more certain that these observations are correct, the tests involving the quantitative determination of the dye absorbed by the polymer were continued with other basic dyestuffs, namely: fuchsine and methylene blue. The test method was the same as before.

The results were as follows:

19.4215 g of polymethyl methacrylate suspended in water, with a molecular weight of 100,000, absorbed 0.1290 g of the dyestuff fuchsine (molecular weight 337) during dyeing, which represents a molar ratio of 1:1.92.

Similar results were obtained in our test of methylene blue; 39.1200 g of emulsion polymethyl methacrylate, with a molecular weight of 96,600, absorbed during dyeing 0.3612 g of the dyestuff methylene blue, which represents a molar ratio of 1:2.2.

TABLE 3

Molar Proportions of Polymethyl Methacrylate and Crystal Violet in Their Reaction During the Process of Suspension Dyeing

Experiment No.	Amount of dyestuff added to 100 ml of aqueous suspension of polymethyl methacrylate, grams	Amount of dyestuff, grams		Quantities of the reacting substances, mols		Quantity of dyestuff absorbed by one mol of the polymer, mols
		Bound by the polymer	Remaining in the filtrate	Polymer	Dyestuff	
1	0.2930	0.2802	0.0928	0.00023	0.00048	2.08
2	0.2631	0.2011	0.0620	0.00024	0.00049	2.01
3	0.1959	0.1771	0.0187	0.00021	0.00043	2.05
4	0.1724	0.1312	0.0412	0.00024	0.00032	1.33
5	0.1482	0.1032	0.0400	0.00024	0.00026	1.05
6	0.1101	0.0835	0.0266	0.00024	0.00020	1.02

Note: Beginning with experiment 5, the coagulation of the polymer was incomplete, owing to an insufficiency of the dyestuff.

Thus, the number of carboxyl groups per mol of polymethyl methacrylate, as found for the acid number, agrees with the number of mols of basic dyestuff (crystal violet, fuchsine, methylene blue) absorbed by the polymer during the process of suspension dyeing. All this indicates that the dyeing of emulsion polymers by aqueous solutions of basic dyes is a chemical process, during which the dye, as a base, reacts with the polymer, as an acid, forming a new and highly stable colored coordination compound. The stability of this coordination compound was later confirmed by its behavior towards solutions of acids and alkalies, and, especially, by its behavior when exposed to light, to which, as we know, aqueous solutions of the basic

dyes themselves, as well as dyes applied to textiles, are not particularly fast.

The tests of the light-fastness of dyed polymethyl methacrylate were made as follows:

The polymethyl methacrylate in suspension was colored with aqueous solutions of basic dyes by the Davankov and Perepelkin method [10,11]. The polymethyl methacrylates, of various colors, were then dissolved in four times the quantity of methyl methacrylate (the monomer), to which 20% dibutyl sulfate by weight of the polymer had been added as a plasticizer. The resulting solution was filtered under pressure through a layer of absorbent cotton and two layers of natural silk. Films 0.2 to 0.4 mm thick were poured off from the filtered solution. Strips of the colored film 50 x 170 mm in size were attached to a sheet of Whatman paper, half of the strip being shielded against the action of light by solid aluminum foil, and were then exposed to a high-pressure quartz lamp (ARK-2), fitted with a spherical reflector. The lamp was mounted 60 cm from the irradiated sheet of paper with the colored films.

For comparison, strips of the same size of natural silk, dyed with the same basic dyestuffs, were attached to the same board.

After 75 hours of quartz-lamp irradiation and exposure to sunlight for half a month in a closed room, all the strips of dyed silk exhibited very great changes in color (bleaching), whereas the films colored with the same dyes, such as methylene heliotrope, crystal violet, malachite green, navy blue, brilliant green, and safranine, showed absolutely no change in hue; the films colored with auramine, rhodamine, methylene blue, and Capri blue exhibited a hardly noticeable change in hue, while noticeable changes were found in the films dyed with Victoria blue and chrysoidine.

The difference between the changes in the color of the silk and the films was greatly enhanced after 125 hours of irradiation.

Thus, coloring polymethyl methacrylate with basic dyes in aqueous suspension results in the formation of a colored coordination compound that is extremely light-fast; this may be due to the chemical reaction of the dye with the polymer, giving rise to a new compound, some of whose properties resemble those of organic lake dyes. They possess one distinguishing feature, however: in contrast to the original basic dyes, they are readily soluble in organic solvents, in which most of the dyes themselves are not soluble, which is apparently due to their chemical structure.

This behavior of polymethyl methacrylate toward aqueous solutions of the basic dyes was checked and confirmed for a number of other emulsion polymers, namely: polystyrene, polyvinyl chloride, copolymers of vinyl acetate and methyl methacrylate, and the like.

SUMMARY

1. Emulsion polymers exhibit selective adsorption and adsorb only basic dyes from aqueous solutions.

2. One dye may be separated from another by the use of synthetic resins.

3. The coloring of finely dispersed polymers by aqueous solutions of dyes may be regarded as a chemical reaction between the basic dye and the acid polymer. This is borne out by the following facts:

a) The acid nature of emulsion polymers produced in the presence of peroxides as initiators;

b) The coagulation and settling out of the polymer during dyeing;

c) The high light-fastness and resistance to chemical reagents of the colored coordination compounds; and

d) The solubility of the colored polymer in organic solvents (in which the original basic dyes are practically insoluble), producing intensely colored solutions.

LITERATURE CITED

[1] Information Bulletin of the Plastic Chemistry Association (USSR), No. 2 (1935)

[2] Ibid, No. 9-10 (1937).

[3] Org Ind Chem USSR, 4-5, 1214, and No. 9, 498 (1939).

[4] Org.Ind.Chem. USSR, 11, 614 (1939).

[5] Org. Ind.Chem. USSR, 9, 1503 (1940).

[6] Osima, Science Ind., 16, 181 (1941).

[7] Chemical Industry, No 4, 16, 1948.

[8] Petrov, Rutovsky, and Losev. The Technology of Plastics and Synthetic Resins, (1946).

[9] Morgan, Trans. Faraday. Soc., 42, 3-4, 169 (1946).

[10] Davankov and Perepelkin, Author's Certificate No. 73239.

[11] Davankov, Author's Certificate No. 77909.

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DIFFERENCES IN THE REACTIVITY OF SOME POLYOXY COMPOUNDS IN A CUPRAMMONIUM SOLUTION AND ITS VARIATION WITH THE CONCENTRATION OF AMMONIA*

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Not enough work has been done up to the present upon the reactivity of various polyoxy compounds – the simplest, as well as the more complex, including cellulose – to the cuprammonium base in a cuprammonium solution containing various percentages of copper and ammonium, nor on the basic laws controlling the complex process involved in the formation of compounds of copper with polyoxy compounds.

In our opinion, study of this problem is of practical as well as theoretical importance. In this instance, we define reactivity as the ability of the polyoxy compounds to enter into chemical reaction with a cuprammonium base, giving rise to the respective compounds, in a cuprammonium solution. To a certain extent, the number of Cu atoms bound by one mol or monomer (for high molecular compounds) of the polyoxy compound under the given reaction conditions may serve as a quantitative measure of this reactivity. This method of expressing reactivity does not always accurately indicate the chemical properties of these compounds, however, since the number of OH groups (or pairs of groups) in the molecule or monomer of the poloxy compound may vary considerably.

We therefore believe that it is better to express the reactivity quantitatively by the ratio of the number of Cu atoms bound by the polyoxy compound to the number of OH groups (or pairs of OH groups) in the polyoxy compound molecule or monomer. This ratio will be the utilization factor of the OH groups in the formation of the Cu compound with the polyoxy compound under the given conditions.

It is only very recently that special researches have been published on this topic. The information contained in the literature hitherto has been of a fragmentary nature.

In their study of cuprammonium solutions of cellulose and other carbohydrates by the polarimetric method, Messmer and Hess [1] found that different carbohydrates bind different numbers of Cu atoms to the OH groups. Cellulose, for example, binds one Cu atom, to each $C_6H_{10}O_5$ monomer, containing 3 OH groups; hydrocellobial binds 1 atom per 6 OH groups; 2 mols of trehalose, containing 16 OH groups, bind 3 mols of the cuprammonium base, etc.

Hess, Messmer, and Ljubitsch [2] made a study of the rotatory power of cellulose preparations in a cuprammonium solution and found that though the other properties (viscosity, solubility in NaOH solution, etc.) of different preparations (cotton

* Report IV in a series on cuprammonium solutions of cellulose.

cellulose, wood cellulose, so-called "cellulose A", mercerized cotton, and artificial silk) differed very considerably, they all exhibited the same angle of rotation ($\alpha°$).

According to these authors, therefore, various preparations of cellulose prove to be quite identical chemically, notwithstanding their great physical and colloid-chemical differences.

In contrast to these preparations, the angle of rotation of hydrocellulose differs considerably from that of cotton, while that of the cellodextrins differs even more (5.68° and 21.3°, respectively).

Lieser and Ebert [3] investigated the reactivity of simple and more complex polyoxy compounds by precipitating their copper compounds with alcohol from a cuprammonium solution and then making quantitative analyses of the precipitated compounds. They suggested structural formulas for the synthesized compounds, based on the results of these analyses. According to these authors, in every instance part of the copper unites with the OH groups to form compounds of the alcoholate type, the rest of the copper entering into a complex, coordination bond; in nearly every case there is no ammonia in the polyoxy copper compounds.

It should be noted that whereas polyoxy compounds with 3 or 4 OH groups are completely copperized, i.e., add Cu in one way or another to every OH group, copperization is incomplete in the hexoses and hexitols, i.e., not all the OH groups bind Cu. The same is true of the polysaccharides they investigated (maltose, lactose, and cellobiose).

Lieser and Ebert surmise that the reason for this incomplete copperization may be the cyclic structure of these carbohydrates, and the singular position and properties of the glucoside group, as well as the micelle structure of the higher carbohydrates.

It is worthy of note that the Lieser method suffers from one fundamental deficiency: the compounds that are analyzed have been precipitated with alcohol. The composition of these compounds may not be the same as that of the compounds present in the solution after the copperization reaction but before their precipitation from the solution.

Quite recently, Reeves [4] published a series of papers in which he reported the following findings, using polarimetric and conductometric methods. Whenever a chemical reaction takes place between the poloxy compound and the cuprammonium base, the conductivity of the system drops sharply; whenever no reaction occurs, the conductivity remains approximately constant.

Investigations of the aliphatic glycols indicates that propanediol-1,2 causes a sharp change in conductivity, which indicates the formation of a coordination compound at the glycol radical, while trimethylene glycol or propanediol-1,3 ($CH_2OH-CH_2-CH_2OH$), in which the two OH groups are separated by a CH_2 group, exhibits no change in conductivity in a cuprammonium solution; it follows, therefore, that trimethylene glycol belongs to the group of substances that cannot form polycoordination compounds, i.e., are unreactive in a cuprammonium solution.

They also showed that the spatial arrangement of the OH groups within the molecule greatly affects the reactivity of polyoxy compounds.

Reeves advanced the hypothesis that the ability of the OH groups in polyoxy compounds to form coordination compounds is governed by the distance between two OH groups. The distance between two adjacent OH groups also depends upon the angle

between their positions in space.

The glucopyranosides exhibit a higher capacity than aliphatic glycols for forming coordination compounds, this capacity varying with the different methylglucopyranosides as follows: glucosides > galactosides > altrosides > mannosides > gulosides.

Cellulose is a classic example of a substance that forms coordination compounds. According to Reeves, the hydroxyl groups at the 2,3-position in each glucoside radical of cellulose react with the cuprammonium base, forming a soluble coordination compound.

Reeves' conductometric method, though superior to the polarimetric method,* is still a qualitative method, though an extremely reliable and interesting one. It is no more possible to ascertain the quantitative ratios of the reacting substances by this method than by various other methods.

In the present paper we have made a study of the reactivity of some of the simple polyoxy compounds (Rochelle salt, sucrose, glycerol, mannitol, dulcitol, and triethanolamine) and some higher carbohydrates (cellulose and its derivatives) by three parallel methods: a) increasing the solubility of $Cu(OH)_2$ in a NH_3 solution by adding polyoxy compounds; b) polarimetry; and c) spectrophotometry.

As our results indicate, all three methods yield the same answers to the question of the great difference in the reactivity of the substances we investigated.

EXPERIMENTAL

Increase in the Solubility of $Cu(OH)_2$ in Aqueous NH_3 when Polyoxy Compounds Are Added

The dissolution of $Cu(OH)_2$ in an aqueous solution of NH_3 is an equilibrium reaction, as one of the present authors recently reported in detail [5].

When polyoxy compounds are added to a cuprammonium solution that contains an excess of undissolved $(Cu(OH)_2$ in a state of equilibrium, more of the latter begins to dissolve [5,6].

The equilibrium of the reaction:

$$Cu(OH)_2 + mNH_3 \rightleftharpoons [Cu(NH_3)_m]\,(OH)_2 + (M - m)NH_3, \qquad (I)$$

established at the given NH_3 concentration before the polyoxy compound has been added, shifts to the right because part of the cuprammonium base is combined into a chemically more stable Cu compound than the cuprammoniumbase, as expressed by reaction (II):

$$[Cu(NH_3)_m](OH)_2 + \begin{matrix} HCOH^{**} \\ | \\ HCOH \end{matrix} \text{ and } NH_3 \rightleftharpoons \begin{matrix} HC-O \\ | \quad\quad Cu(NH_3)_{m_1}^{***} \\ HC-O \end{matrix} + 2H_2O. \qquad (II)$$

The amount of Cu bound by the polyoxy compound in Equation (II) may be calculated from the difference between the Cu concentrations in the cuprammonium solution when the $Cu(OH)_2$ is dissolved in aqueous NH_3 of constant concentration with and without the addition of polyoxy compounds but with all other conditions the same.

*This method can be used even when neither the original nor the resultant compound possesses any rotatory power

**The glycol group is used as a conventional notation for a molecule of the polyoxy compound.

***The number of NH_3 molecules coordinated to the Cu atom increases as a result of this reaction ($m_1 > m$), as our spectrophotometric investigations have shown

A certain inaccuracy is introduced into this calculation by the circumstance that, besides the true dissolution of the $Cu(OH)_2$ according to Equation (I) and the copperization of the polyoxy compound when it is added to the cuprammonium solution, part of the $Cu(OH)_2$ enters solution in the colloidal state, as we have noted earlier [5], as the result of its peptization, probably by the ammonium and cuprammonium bases. To be sure, the amount of $Cu(OH)_2$ dissolved colloidally will always be approximately the same when the experiments are run under identical conditions. In cuprammonium solutions, this part of the Cu may vary in accordance with many factors and cannot be computed accurately in any manner whatsoever.

But inasmuch as we have no more accurate methods available at the present time for determining the quantity of Cu bound by the polyoxy compound in solution in one way or another, we made use of this simple method.

We called the molar ratio of the amount of Cu bound by the polyoxy compound to the amount of polyoxy compound added, or the ratio of the number of mols of Cu to the number of pairs of OH groups in the molecule or the monomer of the polyoxy compound, the degree of copperization of the given polyoxy compound. The higher this ratio, the higher obviously is the reactivity of the polyoxy compound. The maximum value of the ratio must be: Cu: $\frac{n \cdot OH}{2}$ = 1:1.

This method of estimating the reactivity of polyoxy compounds, like the other methods we used in this research, has this advantage over the methods involving the precipitation of the copperized polyoxy compounds from the solution [3]: the ratio is studied in the solution itself.

The $Cu(OH)_2$ was dissolved in aqueous NH_3 solutions of different concentrations. We ran simultaneous parallel tests under identical conditions with different polyoxy compounds at each concentration of NH_3, as well as a blank test (with no polyoxy compound added); the increase in the solubility of $Cu(OH)_2$ or the increase in the concentration of Cu(ΔCu) is determined by comparison with the blank test results.

The $Cu(OH)_2$ was dissolved in 100-ml measuring flasks with a constant excess of $Cu(OH)_2$* at a constant temperature of 20°, which was maintained by means of a thermostat. After dissolution had continued for 2 hours, the excess $Cu(OH)_2$ that had not dissolved was separated from the solution by means of a glass filter, the surface of which was covered with a layer of asbestos. The percentage of Cu and NH_3 in the filtered solution was determined by analysis. The percentage of Cu was determined iodometrically, with a CNS ion added to diminish the solubility of the Cu_2I_2 and increase the analytical precision. The percentage of NH_3 was determined by titrating back with a 1.0 N solution of H_2SO_4.

The results of our determinations of the solubility of $Cu(OH)_2$ at various concentrations of NH_3, with various polyoxy compounds added, and the determinations of the degree of copperization as a function of the NH_3 concentration and the nature of the additive, are listed in the subjoined table and are shown by the respective curves in Figs. 1, 2, 3, and 4.

The table gives figures for the solubility of $Cu(OH)_2$ at a single concentration of NH_3 for seven samples of polyoxy compounds.

Figure 1 gives the curves showing the increase in the solubility of $Cu(OH)_2$ as a function of the NH_3 concentration, with and without the addition of polyoxy compounds. The curves of Fig. 1 exhibit a continuous rise in the $Cu(OH)_2$ solubility as the concentration of NH_3 is increased. The curves for the changes of the Cu concentration with various polyoxy compounds added lie higher than the curve of $Cu(OH)_2$ solubility without any additive.

*The size of the excess of $Cu(OH)_2$ affects the solubility of the $Cu(OH)_2$, as we had ascertained previously [7].

Degree of Copperization of Various Polyoxy Compounds at a NH_3 Concentration of 200.0 Grams/Liter; t = 20°

No.	Polyoxy compound	Quantity added, mols/liter	Cu concentration, mols/liter	Increase in Cu concentration (ΔCu), mols/liter	Molar ratio of bound Cu to quantity of polyoxy compound added	Degree of copperization of the polyoxy compound $\left(Cu: \frac{n \cdot OH}{2}\right)$
1	Rochelle salt	0.020	0.1772	0.0340	1.7	1.700
2	Dulcitol	0.020	0.1861	0.0429	2.15	0.717
3	Mannitol	0.020	0.1826	0.0394	1.97	0.657
4	Glycerol	0.020	0.1682	0.0250	1.25	0.833
5	Triethanolamine	0.020	0.1682	0.0250	1.25	0.833
6	Cellulose	0.091	0.2166	0.0698	0.77	0.530
7	Oxycellulose	0.095	0.2291	0.0828	0.87	0.580

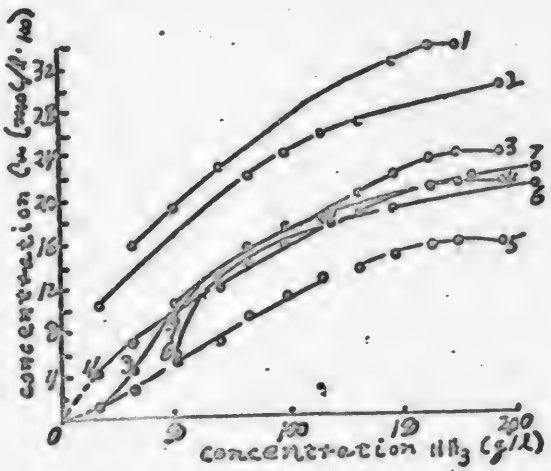

Fig. 1. Solubility of $Cu(OH)_2$ in NH_3 solutions of various concentrations with various polyoxy compounds added.

1-Rochelle salt (0.125 mol/liter); 2-Rochelle salt (0.10 mol/liter); 3-hydrocellulose (0.10 mol/liter); 4-sucrose (0.05 mol/liter; 5-with no additive. 6-cellulose (0.091 mol/liter); 7-oxycellulose (0.095 mol/liter).

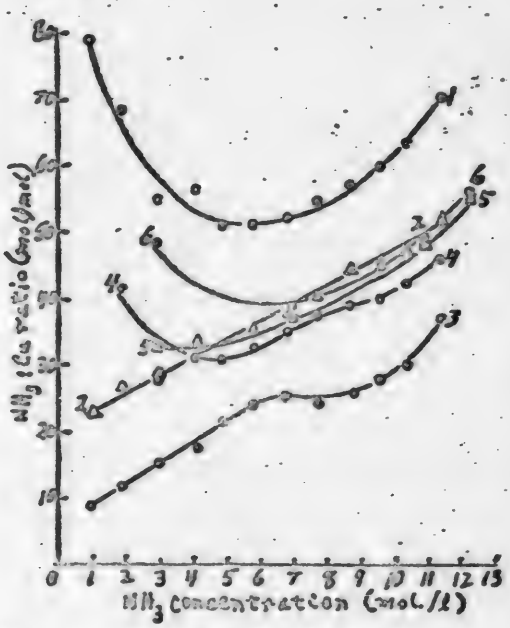

Fig. 2. Change in the NH_3:Cu ratio with a change in the concentration of NH_3 in solution as affected by the addition of polyoxy compounds.

$Cu(OH)_2$ + NH_3 solutions: 1-with no additive; 2-with sucrose added (0.05 mol/liter); 3-with Rochelle salt added (0.100-0.125 mol/liter); 4-with hydrocellulose added (0.10 mol/liter); 5-with oxycellulose added (0.095 mol/liter); 6-with cellulose added (0.091 mol/liter).

The changes in the solubility of $Cu(OH)_2$ when cellulose or hydrocellulose is added at NH_3 concentrations ranging up to 3 N are worthy of note. At an NH_3 concentration of 16.8 grams/liter, the solubility does not increase when hydrocellulose is added; only at higher concentrations do we find any appreciable increase in the concentration of Cu in the solution. When the NH_3 concentration is approximately 3.0 mols per liter, adding cellulose results in only a slight increase in the solubility, whereas the addition of oxycellulose or hydrocellulose, not to mention the other polyoxy compounds, produces a considerable increase in the $Cu(OH)_2$ solubility at this concentration.

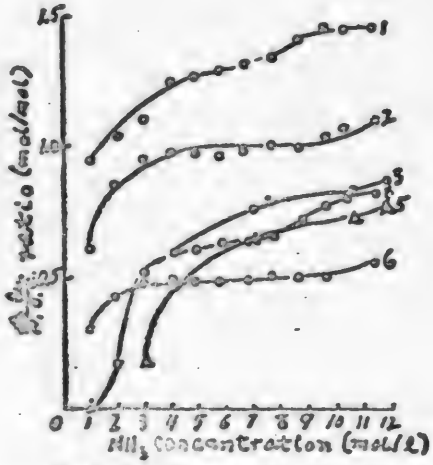

Fig. 3. Change in the degree of copperization of various polyoxy compounds (p.o.c.) with the ammonia concentration.

Polyoxy compounds: 1-Rochelle salt (0.100-0.125 mol/liter); 2-sucrose (0.05 mol/liter); 3-oxycellulose (0.095 mol/liter); 4-hydrocellulose (0.10 mol/liter); 5-cellulose (0.09 mol/liter); 6-sucrose, degree of copperization of each part of the sucrose disaccharide.

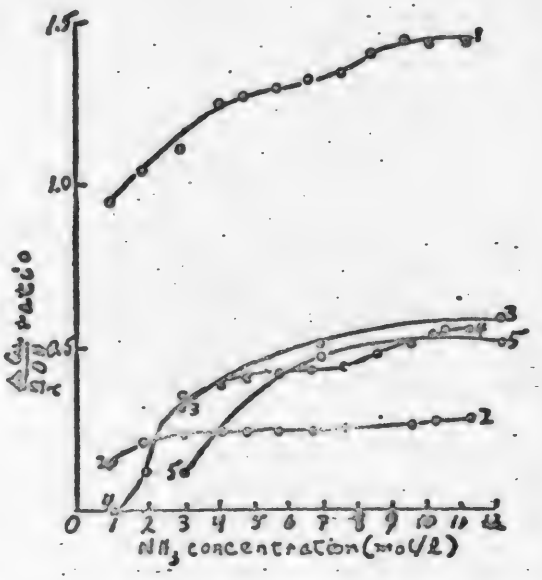

Fig. 4. Degree of copperization of various polyoxy compounds as a function of the NH_3 concentration, calculated from the number of OH groups per molecule.

Polyoxy compounds: 1-Rochelle salt (0.100-0.125 mol/liter); 2-sucrose (0.05 mol/liter); 3-oxycellulose (0.095 mol/liter); 4-hydrocellulose (0.10 mol/liter); 5-cellulose (0.091 mol/liter).

Fig. 2 gives the curves showing the change in the NH_3:Cu ratio (mol/mol) at various NH_3 concentrations as affected by various additives.

The curves are not alike. Curve 1, for a solution containing no polyoxy compound, lies above all the other curves and has a minimum at an NH_3 concentration of 5-6 mols/liter. Curve 2, for a solution with sucrose added, is a straight line that exhibits a continuous rise of the NH_3:Cu ratio as the NH_3 concentration is increased and lies far below Curve 1. Curve 3, for a solution to which Rochelle salt has been added, is still lower; it starts out as a straight line, but bends away at NH_3 concentrations ranging from 6 to 9 mols/liter. Curves 4 and 6, for hydrocellulose and

cellulose, respectively, both exhibit minima, the hydrocellulose curve lying below the oxycellulose and cellulose curves. The minima of Curves 4 and 6 correspond approximately to the NH_3 concentration at which the minimum of Curve 1 is located.

The curves of Fig. 3 show the change in the degree of copperization of various polyoxy compounds as a function of the concentration of NH_3 in the solution. All the exhibit a rise in degree of copperization with rise in NH_3 concentration in the solution. The nature of these curves differs, however. Whereas with sucrose (2), the degree of copperization rises sharply only after the NH_3 concentration has reached 4 mols per liter, the degree of copperization rises continuously with cellulose (5) or Rochelle salt (1); the rise in the degree of copperization is again faster at the start, to be sure, and slower toward the close.

Curve 6, for a sucrose solution adjusted for one part or one molecule of the monosaccharide, lies above Curves 4 and 5, for cellulose and hydrocellulose, respectively, only at NH_3 concentrations below 3.0 mol/liter; above this concentration the curve lies below all the others, indicating that the degree of copperization of sucrose is lower than the degree of copperization of cellulose or its derivatives at these concentrations of NH_3.

Figure 4 gives the curves showing the computed change in the degree of copperization, based on the number of OH groups or, more exactly, the number of pairs of OH groups per molecule of the polyoxy compound. The curves are of the same shape as in Fig. 3. As in Fig. 3, the highest curve of all is that for Rochelle salt. Only at NH_3 concentrations below 2 mols/liter does curve 2, for sucrose, lie above Curves 4 and 5 for cellulose and hydrocellulose, respectively; at NH_3 concentrations higher than 2 mols per liter this curve lies below the curves for cellulose, oxycellulose, and hydrocellulose.

Polarimetric Investigations

We know [7,8] that the reaction of some polyoxy compounds* with a cuprammonium solution causes a more or less pronounced change in the angle of rotation of the plane of polarization of transmitted light. The onset, nature, and magnitude of these changes in the angle of rotation may serve as a qualitative and quantitative index of the reactivity of polyoxy compounds.

The rotatory power of filtered cuprammonium solutions of polyoxy compounds was determined in a Lippich polarimeter. A mercury-quartz lamp was used as a light source in order to increase the proportion of blue and violet light in the emitted spectrum and to provide better light transmission through strongly absorptive, intensely colored solutions. To make the solutions more translucent, the measurements were made in short tubes 2 cm long.

In the polarimetric analysis of solutions of Rochelle salt and sucrose, which exhibit rotatory power even in aqueous solutions, an increase in their rotatory power (due to a reaction with the cuprammonium base) was detected by comparing the angles of rotation of solutions of these polyoxy compounds in aqueous, aqueous ammonia, and cuprammonium solutions, of identical concentration.

In the investigation of cuprammonium solutions of hydrocellulose, the angle of rotation was determined by comparing the rotatory power of this solution with that of the cuprammonium solution without any polyoxy compound added, since we know that solutions of cellulose in acids or alkalies (with the sole exception of a cuprammonium solution) have practically no rotatory power of their own.

The results of our investigations of the rotatory power of some polyoxy compounds

*Provided the polyoxy compound is not a racemic mixture.

in a cuprammonium solution at various concentrations of NH_3 are shown by the curves in Fig. 5. In each case, the curves exhibit an increase in the rotatory power of cuprammonium solutions of the polyoxy compounds as the NH_3 concentration is increased.

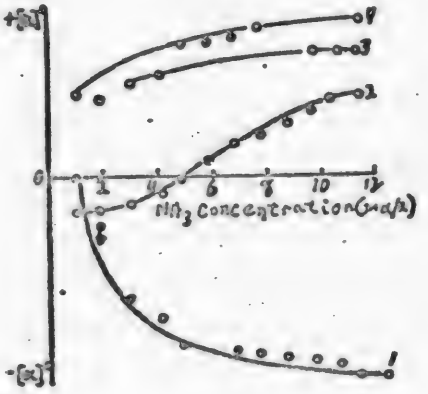

Fig. 5. Changes in the rotatory power of cuprammonium solutions of polyoxy compounds at various concentrations of ammonium and of the polyoxy compound.

1-Hydrocellulose (0.10 mol/liter); 2-sucrose (0.05 mol/liter); 3-Rochelle salt 0.125 mol/liter); 4-Rochelle salt (0.200 mol/liter).

Curve 1 indicates that no change is observed in the rotatory power of a solution of hydrocellulose up to an NH_3 concentration of approximately 1 mol/liter, and that only at concentrations above 2 mols/liter is a sharp increase in the rotatory power observed, this increase continuing up to an NH_3 concentration of 5 mols/liter, above which the increase in the rotatory power begins to slow down. Curves 2, 3, and 4 show that solutions of Rochelle salt and sucrose exhibit a considerable increase in rotatory power even at low concentrations of NH_3. As the NH_3 concentration is raised, the rotatory power continues to increase, faster in the sucrose solution than in the solution of Rochelle salt.

Spectrophotometric Investigations

As part of the cuprammonium base is bound in accordance with Equation (II), as shown above, the degree of amination, or the number of NH_3 molecules coordinated to the Cu atom, increases.

A change in the degree of amination or in the inner sphere within the complex copper cation must cause a change in color and, consequently, in the coefficient of molecular absorption of the copper solution. And the greater these changes, the more will the molecules of the cuprammonium base evidently have entered into reaction with the polyoxy compound. Hence, we think it possible to estimate the reactivity of polyoxy compounds qualitatively by the change in Em, the coefficient of molecular absorption.

These researches, like those using the polarimetric method, were made with filtered solutions, whose Cu and NH_3 content had been determined by analysis. The coefficient of molecular absorption, Em, was measured with a Koenig-Martens spectrophotometer by a method resembling the one described by Fedorov [9]. The light for the spectrophotometer came from a 200-watt electric bulb. The Em was measured by monochromatic light, with a wavelength λ of 541.6 mμ, corresponding to the green Hg line in the spectrum. The Em was calculated from the formula

$$Em = \frac{\log \tan \alpha_1 - \log \tan \alpha_2}{l \cdot C}$$

where α_1 and α_2 are the deflection angles until the fields of view are equal, in degrees; l is the thickness of the solution layer of the length of the cell, in centimeters; and C is the concentration of copper in mol/liter.

The deflection angles α_1 and α_2 were measured at least 10 times, the mean value being used in calculating Em from the above formula. Measurements were made in the

the first and fourth quadrants for each solution. In every case the cell was 2 cm long.

The results of our spectrophotometric investigations are given by the curves in Fig. 6.

All the curves exhibit a fairly sharp decrease in Em with the NH_3 concentration in a cuprammonium solution and with the addition of polyoxy compounds. Different additives diminish Em differently at different concentrations of NH_3.

Adding Rochelle salt (4) or sucrose (3) lowers the Em even when the NH_3 concentration is approximately 1 mol/liter, whereas adding hydrocellulose (2) produces practically no change in the magnitude of the Em at this concentration.

As the concentration of NH_3 in the solution rises to 4-6 mols/liter, the difference between the Em of the cuprammonium solution with no additive and with Rochelle salt or sucrose added diminishes, on the one hand, while the analogous difference between the cuprammonium solution with no additive and with hydrocellulose added increases, on the other; as the concentration of NH_3 is increased still further, the differences between the values of Em become smaller for all the solutions.

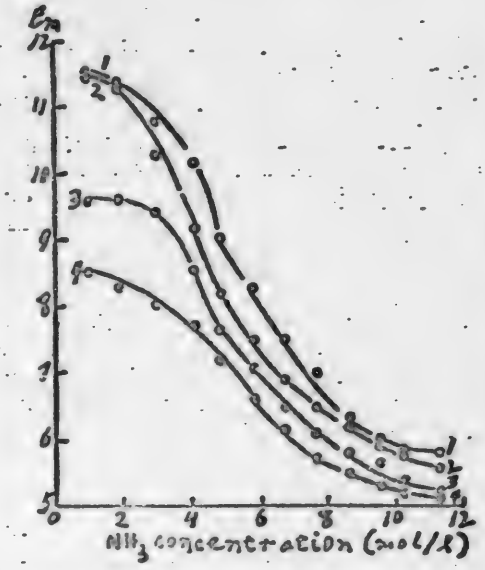

Fig. 6. Change in the coefficient of molecular absorption as a function of the concentration of NH_3 and the addition of polyoxy compounds. λ = 541.6 mμ.

Cuprammonium solutions: 1-with no additive; 2-with hydrocellulose added (0.1 mol/liter); 3-with sucrose added (0.05 mol/liter); 4-with Rochelle salt added (0.100-0.125 mol/liter).

Evaluation of Results

When $Cu(OH)_2$ is dissolved in aqueous NH_3, a cuprammonium base is formed in accordance with the equilibrium Equation (I). As the concentration of NH_3 in the solution is increased, the equilibrium of Reaction (I) is shifted to the right: the concentration of Cu in the solution is raised, rapidly at first, but slowing down at NH_3 concentrations > grams/liter (Fig. 1).

Formation of a cuprammonium base requires a large excess of NH_3; the NH_3:Cu (mol/mol) ratio varies with the concentration of NH_3 in the solution, dropping sharply at first, reaching a minimum at a concentration of 5-6 mols/liter, and then rising again.

The diminution in the NH_3:Cu ratio is apparently due to the fact that as the NH_3 concentration rises, the relative increase in the concentration of Cu in the solution is more rapid than the rise in the NH_3 concentration, i.e., increasing the NH_3 concentration to 5-6 mols/liter greatly favors Reaction (I). Increasing the NH_3 concentration to above 5-6 mols/liter entails a rise in the NH_3:Cu ratio (Fig. 2), which may be explained as due to a decrease in the degree of dissociation of the cuprammonium base and a diminution of its chemical stability [5].

When polyoxy compounds are added to a cuprammonium solution, the equilibrium Reaction (II) takes place (provided the excess of $Cu(OH)_2$ remains unchanged *), the corresponding Cu compound being formed.

The compound formed is apparently more stable chemically and is less dissociated or not dissociated at all into ions, its stability depending upon the nature of the polyoxy compound. New batches of Cu take the place of the Cu departing from the equilibrium of Reaction (I), resulting in the dissolution of a corresponding amount of $Cu(OH)_2$ in the NH_3 solution in accordance with Reaction (I).

These processes continue until the equilibrium of Reactions (I) and (II) has been established. Hence, these two reactions are conjugate reactions, as it were. Reactions (I) and (II) result in an increase in the concentration of Cu in the solution, the larger the quantity of additive and the higher the reactivity of the compound added, the greater being the increase. Thus, the rise in the Cu relative to the quantity of the polyoxy compound added enables us to judge the reactivity of a given polyoxy compound.

The data reproduced in the table and in the form of curves in Figs. 3 and 4 indicate that the degree of copperization rises with an increasing concentration of NH_3 in the solution for all the polyoxy compounds tested by us.

But the position of these curves on the graphs and their nature, as well as the tabular data, point to the great differences in the degree of copperization of the various polyoxy compounds.

Comparison of Figs. 3 and 4 shows that the degree of copperization likewise depends upon how it is computed. For example, when the degree of copperization is calculated in mols of Cu (of the base) per mol (or monomer) of the polyoxy compounds, as indicated in Fig. 3, sucrose is in second place as far as degree of copperization is concerned, behind Rochelle salt (2); when it is computed for each part of the sucrose disaccharide (6), at high NH_3 concentrations, sucrose is in last place, behind cellulose and its derivatives.

When we compute the degree of copperization on the basis of the number of OH groups in the molecule or monomer of the polyoxy compound, we get the same sequence of these polyoxy compounds in terms of their degree of copperization: the curves for cellulose and its derivatives and for sucrose fall even lower.

According to the data in the Table and in Figs. 3 and 4, all the polyoxy compounds may be arranged in the following order of decreasing degree of copperization (at high NH_3 concentrations), computed in mols per mol:

Dulcitol > mannitol > Rochelle salt > glycerol, triethanolamine > sucrose > oxycellulose > cellulose.

Making this computation on the basis of each pair of OH groups, we get a different series, in which Rochelle salt holds first place:

Rochelle salt > glycerin, triethanolamine > dulcitol > mannitol > oxycellulose > cellulose > sucrose.

The most accurate way of expressing the degree of copperization quantitatively is the method based upon the number of hydroxyl groups in the molecule or monomer of the polyoxy compound.

The relatively low degree of copperization of sucrose at high ammonia concentrations is worthy of note.

The difference in the degree of copperization may be also seen in the change

*The solubility of $Cu(OH)_2$ depends upon the amount of excess $Cu(OH)_2$ for any given concentration of NH_3 and with all other conditions remaining the same. [6].

in the NH_3:Cu ratio (Fig. 2) as polyoxy compounds are added to a cuprammonium solution.

The sharp drop in this ratio when Rochelle salt or sucrose is added, even at low NH_3 concentrations, is evidently due to the fact that these polyoxy compounds are relatively more reactive and, at low NH_3 concentrations form chemically more stable compounds with copper that are not hydrolyzed even at low NH_3 concentrations. The further increase in the NH_3:Cu ratio may be due to the fact that the rise in the Cu concentration lags behind the rise in the NH_3 concentration as copperization increases.

The slighter decrease in this ratio when cellulose and its derivatives are added is due to the much lower reactivity of these preparations, especially at low NH_3 concentrations.

This is illustrated by the curves in Fig. 1.

As the concentration of NH_3 rises, the reactivity of cellulose and its derivatives increases sharply, and the chemical stability of the copper compounds that are formed apparently rises, thus raising the degree of copperization.

The differences in the reactivity of the polyoxy compounds are likewise shown by our polarimetric and spectrophotographic researches (Figs. 5 and 6).

The greatest difference in reactivity is displayed by hydrocellulose at one end and Rochelle salt and sucrose at the other. The latter two compounds exhibit large changes of rotatory power and of the ability to absorb light of a specific wave length even at low NH_3 concentrations, while the hydrocellulose solution displays neither rotatory power nor any change in the light-absorptive capacity of the solution.

The reactivity of hydrocellulose rises as the NH_3 concentration is increased. Hence, increasing the concentration of NH_3 in a cuprammonium solution favors the occurrence of Reaction (II), shifting the equilibrium to the right, as previously noted [8-11].

The increase in the degree of copperization of polyoxy compounds or the increase in their reactivity toward the cuprammonium base as the NH_3 concentration is raised may be due, on the one hand, to an increase in the concentration of OH ions (a rise in the pH of the solution) and a related increase in the chemical stability of the resulting Cu compound, as a result of which the equilibrium of Reaction (II) is shifted to the right, and on the other, to an increase in the degree of amination of the Cu in the cuprammonium base (an increase in the number of NH_3 molecules coordinated with the Cu atom), an increase in the strength of the base, and a rise in its reactivity.

The differences between the reactivity of the various polyoxy compounds may be due to the relative complexity of the polyoxy compound's molecule, to differences in the configuration of these molecules, or to different arrangements of their hydroxyl groups.

The degree of copperization of the polyoxy compounds we have investigated does not reach the theoretical value (1 Cu:2 OH groups), except in the case of Rochelle salt. The exceptionally high degree of copperization of Rochelle salt (higher than the theoretical value) may, we believe, be due to the fact that at high values of pH an equilibrium is set up between the Rochelle salt already copperized and the cuprammonium base, with K^+ and Na^+ cations displaced from the salt and partially

replaced by the complex copper cation $[Cu(NH_3)_m]^{++}$.

The fact that at high NH_3 concentrations the reactivity of sucrose is lower than that of cellulose, which consists essentially of glucose anhydrides, indicates that the reactivity of the fructose part of the sucrose is much lower than that of the glucose part.

On the other hand, the high reactivity of sucrose at low concentrations of NH_3 justifies the assumption that the glucose part of the sucrose is much more reactive than the glucose radical of cellulose, which may be explained by the great difference between the molecular weights of these substances.

SUMMARY

1. Polyoxy compounds possess varying reactivity to a cuprammonium base, depending, apparently, on the molecule's size, the complexity of its structure, and its configuration, and upon the mutual spatial positions of the reactive pairs of hydroxyl groups.

The simplest polyoxy compounds (glycerol, Rochelle salt, etc.) enter into reaction with the cuprammonium base even at low concentrations of ammonia, whereas cellulose and its derivatives (oxy- and hydrocellulose) do not react with the cuprammonium base at NH_3 concentrations that are below 3.0 mols/liter.

2. Ammonia plays an important part in the reaction of cellulose with the cuprammonium base. Raising the concentration of ammonia in the cuprammonium solution increases the reactivity of polyoxy compounds, especially cellulose and its derivatives, which may be due, on the one hand, to an increase in the pH of the medium, and on the other, to an increase in the degree of amination of the copper and a change in the physico-chemical properties of the cuprammonium base.

3. The formation of a compound of copper with a polyoxy compound involves an increase in the degree of amination of the copper bound to the polyoxy compound.

LITERATURE CITED

[1] E.Messmer, K.Hess. Z. physik. Chem., 126, 369-416 (1927).

[2] K.Hess, E.Messmer, Ljubitsch, Ann. chim., 144, 287-327 (1926).

[3] Th. Lieser, R.Ebert, Ann. chim., 532, 89 (1937); 528, 276 (1937).

[4] R.Reeves, J.Am. Chem.Soc., 71, No. 1, 209 (1949); No. 1, 212 (1949).

[5] M.I.Arkhilov, J.Appl. Chem., 21, 3, 235 (1948).

[6] M.I.Arkhilov and A.B.Pakshver, J.Appl.Chem. 16, 11-12, 356 (1943).

[7] K.Hess. The Chemistry of Cellulose and Its Companions, 204-206. United Scientific and Technical Press, State Chemical Press, Leningrad (1934).

[8] M.I.Arkhilov and V.P.Kharitonova, J.Appl. Chem. 22, 7, 761 (1949).

[9] N.T.Fedotov. A Course in the Principles of Light, 51. United Scientific and Technical Press, Moscow (1935).

[10] M.I.Arkhilov and V.Kharitonova, J.Appl. Chem. 22, 9, 1030 (1949).

[11] K.Hess. The Chemistry of Cellulose and Its Companions, 192. United Scientific and Technical Press, Leningrad (1934).

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A STUDY OF γ-PYRONECARBOXYLIC ACID AND ITS TRANSFORMATIONS*

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The wastes of opium manufacture readily yield meconic acid, which can be converted by boiling with hydrochloric acid (sp. gr. 1.13) into comenic acid, while treating the latter with aqueous ammonia yields comenamic acid.

Comenamic acid and its derivatives have been the subject of investigation for a fairly long time by several authors (How [1], Reibstein [2], Verkade [3], Garkusha [4], and others). Throughout the literature, including the handbooks, comenamic acid is assigned the structure of 4,5-dihydroxypicolinic acid.

The author, starting with the structure of meconic acid and the paper by Peratoner and Tamburello [5], expressed the hypothesis in his previous paper [6] that comenamic acid is 3,4-dihydroxypyridinecarboxylic acid-2, rather than 4,5-dihydroxypyridinecarboxylic acid-2.

Our research now enables us to assert that comenamic acid actually has the structure of 3,4-dihydroxypyridinecarboxylic acid-2.

This is proved by the fact that decarboxylation of comenamic acid yields dihydroxypyridine, whose properties and melting point are identical with those of the 3,4-dihydroxypyridine synthesized by sulfonating pyridine and then fusing the product with caustic alkali. A test sample of the dihydroxypyridine prepared from comenamic acid exhibited no depression of the melting point when mixed with 3,4-dihydroxypyridine.

Our decision to synthesize the diethyl hydrochloride of 3,4-dihydroxypicolinamide and the diethyl hydrochloride of comenamide was motivated by the following factors:

1) The availability of comenic acid and comenamic acid, as the initial materials:

2) The unavailability to us of literature describing the synthesis of diethyl

*Report II of a series on this topic.

comenamide and diethyl 3,4-dihydroxypicolinamide.

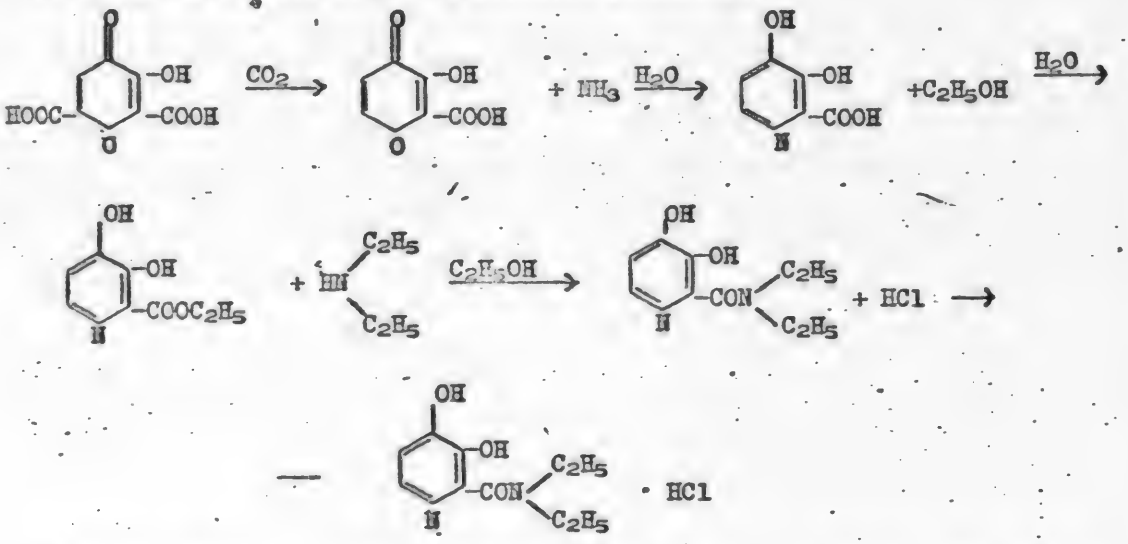
3) The similarity of the structure of the diethyl 3,4-dihydroxypicolinamide to that of nicotinic acid.

Nicotinic acid, like its derivatives, has been employed widely in medicine.

In the light of all this, we assumed that the diethyl hydrochloride of 3,4-dihydroxypicolinamide might also find application in medicine. Preliminary pharmaceutical tests of this preparation indicated that it actually is a pharmacologically active substance [7].

The raw material for the synthesis of the diethyl hydrochloride of 3,4-dihydroxypicolinamide consisted of the wastes of opium manufacture: meconates. The meconates were first treated with chloroform to remove coloring substances, after which meconic acid was recovered from them via its ammonium salt. The meconic acid was converted into comenic acid, and then into comenamic acid. Ethyl comenamate was secured by reacting comenamic acid with absolute alcohol in the presence of hydrogen chloride. The ethyl comenamate was treated with diethylamine, and then saturated with hydrogen chloride.

The overall synthesis may be represented as follows:

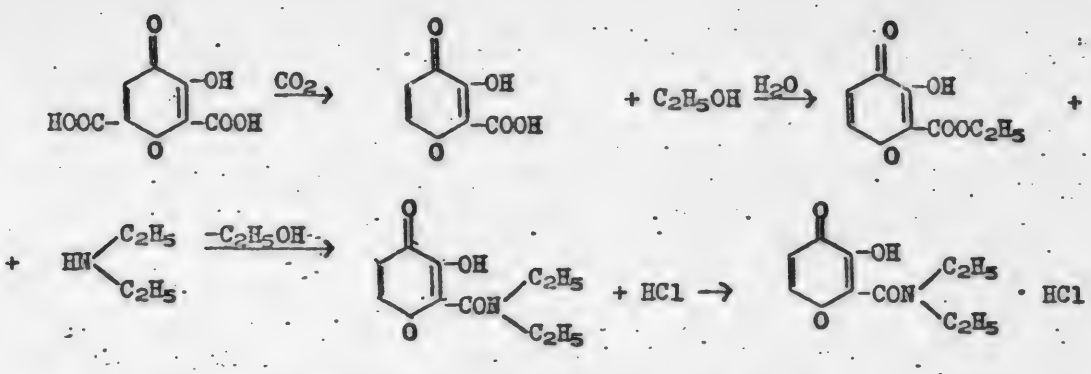


Our experimental investigations established that this synthesis can be simplified: synthesizing comenamic acid from meconic acid directly.

The diethyl hydrochloride of 3,4-dihydroxypicolinamide differs from "cordiamine" in that its amide group is not at the β-position but that the α-position, with hydroxyl groups introduced at the β,γ-positions.

The diethyl hydrochloride of comenamide was synthesized as follows: meconic acid - comenic acid - the latter's ethyl ester - diethyl comenamide - diethyl hydrochloride of comenamide.

This synthesis may be represented as follows:



This synthesis proceeds smoothly and with high yield in all its stages. Pharmacological tests of this preparation on an isolated frog's heart produced an action opposite to that of "cordiamine"; it is a toxic substance.

EXPERIMENTAL

We have described the synthesis of meconic acid from the "meconates" and its purification, and the preparation of comenic acid previously [8], so that we need not dwell on it here.

Synthesis of comenamic acid from meconic acid. 50 g of meconic acid is treated with 150 ml of concentrated ammonia in a chemical beaker, carefully stirred, and cautiously heated over an alcohol burner. When there is only little liquid left in the beaker, some water is added, and the whole is boiled until no more carbon dioxide is evolved; this causes ammonium comenamate to precipitate out. The residue is diluted with water and heated to dissolve the salt, after which the hot solution is filtered through a Buchner funnel.

A 10% solution of hydrochloric acid is added to the filtrate until it is slightly acid (with Congo), after which it is allowed to stand overnight. The precipitated comenamic acid is filtered through a Buchner funnel, washed with cold water until it no longer exhibits a reaction for the chlorine ion, and dried in air.

The synthesized comenamic acid consists of dark-brown platelets with a melting-point of 260-262°. Yield 34.6%.

Synthesis of ethyl comenamate. 350 ml of absolute alcohol is added to 50 g of comenamic acid, an anhydrous hydrogen chloride is passed through the resulting mixture until the saturation point is reached. The reaction mixture warms up during this process, so that we have to cool the flask with cold water.

When saturation is complete, the solution is filtered, and the alcohol is driven off. The residue left behind is neutralized with a 10% ammonia solution until its reaction is neutral (the ester dissolves in an excess of ammonia). The precipitated ester of comenamic acid is filtered out and washed with cold water until it no longer exhibits a reaction for the chlorine ion, and dried in air.

It consists of light-brown crystals with a melting point of 204-205°. Yield - 40.2%.

Synthesis of the diethyl hydrochloride of 3,4-dihydroxypicolinamide. 125 ml of diethylamine is poured over 25 g of ethyl comenamate. The mixture is carefully stirred for an hour and then set aside to stand overnight. Then the excess diethylamine is decanted from the precipitate, and the latter is dried in air. The dried

precipitate is dissolved in a small quantity of absolute alcohol. Dry hydrogen chloride is passed through this solution until saturation (this causes the solution to heat up considerably).

After the solution cools, sulfuric ether is added to it, and the whole is allowed to stand overnight. Then the solution is decanted from the precipitate, and the tarry impurities are removed from the latter. This is done by dissolving the precipitate of diethyl hydrochloride of 3,4-dihydroxypicolinamide in a small quantity of alcohol. It dissolves quite readily. Then a small amount of sulfuric ether is added to the solution. The black precipitate that settles is filtered out.

A small quantity of sulfuric ether is again added to the filtrate - tar separates out; the solution is separated from the tar by decantation. This operation is repeated several times. When no more tar can be recovered from the solution, an excess of sulfuric ether is added to the latter, and the solution is set aside overnight in the cold for crystallization to take place. The resulting crystals are filtered out and washed with sulfuric ether.

The diethyl hydrochloride of 3,5-dihydroxypicolinamide is a cream-colored, crystalline powder, which is readily soluble in water and alcohol, but insoluble in ether or benzene. Melting point: 159°. Yield: 13.3%.

Synthesis of ethyl comenate. 400 ml of absolute alcohol is added to 50 g of comenic acid. It is heated over a water bath with a reflux condenser while a stream of anhydrous hydrogen chloride is passed through it until it is saturated.

After the solution has cooled, the alcohol is driven off, and the crystals that settle are filtered out, washed with ice water, and recrystallized from water.

Recrystallization yields lustrous, white, acicular crystals that are readily soluble in aqueous ammonia, and less readily so in water. They dissolve in hot alcohol. Melting point: 127°. Yield: 40.6%.

Synthesis of the diethyl hydrochloride of comenamide. 250 ml of diethylamine is poured over 50 g of ethyl comenate. The mixture is carefully stirred for one hour and then set aside to stand overnight. Then the excess diethylamine is decanted from the precipitate, which is dried in air. The dried precipitate is dissolved in a small amount of absolute alcohol, and anhydrous hydrogen chloride is passed through the solution. Then sulfuric ether is added until the mixture turns cloudy, and it is set aside to stand overnight. The crystals that form are filtered out and washed with sulfuric ether.

This yields greenish-yellow crystals that are readily soluble in water and less so in alcohol, but are insoluble in ether. Melting point: 168°. Yield: 49.5%. The crystals of the diethyl hydrochloride of comenamide turn dark, deliquesce, and decompose when exposed to the air for a long time.

SUMMARY

1. Comenamic acid is 3,4-dihydroxypryidinecarboxylic acid-2.

2. A new pyridine derivative - the diethyl hydrochloride of 3,4-dihydroxypicolinamide - has been synthesized and described.

3. A new pyran derivative - the diethyl hydrochloride of comenamide - has been synthesized and described. The crystals of the diethyl hydrochloride of comenamide decompose when exposed to the air.

LITERATURE CITED

[1] How, Ann., 80, 65, 91 (1851).

[2] Reibstein, J. prakt. chem., 24, 284 (1924).

[3] Verkade, Rec. trav. chim., 43, 886 (1924).

[4] Garkusha, J. Gen. Chem., 16, 2025 (1946).

[5] Peratoner, Tamburello, Zbl., 36, 1, 56 (1906).

[6] Belonosov, J. Appl. Chem. 22, 1103 (1949).

[7] Belonosov and Makarevich, Biochemistry, 14, 441 (1949).

Received March 16, 1950.

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